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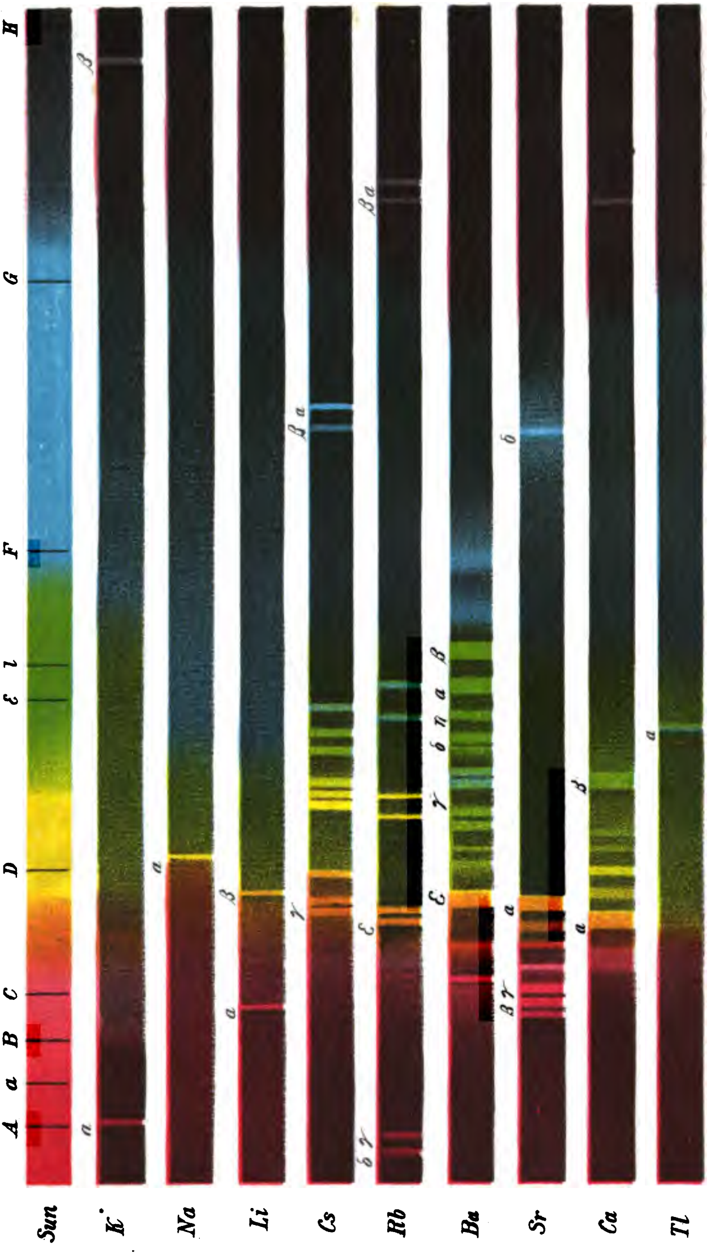
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THE ELEMENTS

OF

CHEMISTRY.

BY

SIDNEY A. NORTON, A. M., M. D.,
PROFESSOR IN THE OHIO AGRICULTURAL AND MECHANICAL COLLEGE.

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PREFACE.

THIS work is intended as a text-book, not as a manual for reference. The author has endeavored to select such chemical phenomena as represent the cardinal principles of the science, giving preference to those which are easily reproduced by the student, and which enter into the affairs of common life. To attain this end, he has omitted many excellent experiments which require the use of expensive apparatus, and has substituted others which, if less "classical," are of easier application.

The engravings represent well-fashioned apparatus; but no one ought to be deterred from attempting an experiment because he has not the exact shaped figure. Any drug-store or kitchen will afford bottles and tumblers, which may be used in place of flasks and beakers. In some way, the experiments ought to be tried. Glass tubing, rubber tubing, and good corks are the first requisites, and are easily obtainable. The most essential thing in experimenting is the experimenter. He should know (1) what he proposes to do; (2) what are the means at his command; and (3) how he intends to use them. He must bear in mind that a Chinese fidelity is not required — *e. g.*, that one alkali may replace another, or that corresponding salts may be substituted one for another as occasion requires. Nevertheless, he must remember that Chemistry is exact in her methods; (1) that careless manipulation will not secure good results; and (2) that such words as neutral, acid, basic, excess, must not be neglected.

As regards nomenclature, the author has followed the excellent example of Dr. Odling, viz, to use those names which have become a part of our language with as little change as possible, and the newer names for those substances which concern chemists only.

As regards notation, it must be borne in mind that all formulæ are alike subject to change. No greater mistake can be made than that any formula (except a binary) tells the whole truth about a molecule, or that any formula which correctly represents the percentage composition of a substance may not be, at times, available in fixing in the mind of the student the fact to be remembered. The author has, therefore, used the formula that appeared convenient at the time; and feels that an experience of twenty years' teaching warrants him in advising his fellow-teachers not to attempt to place theory above practice. The use of theory is to enable one to generalize known facts and predict new ones; the business of teaching is to enable the student to master facts, principles, and laws already ascertained and established.

The science of chemistry is not an easy one; but it is hoped that the portion of it here presented will meet the wants of both teacher and student in the selection of facts and the method of presentation.

The author's thanks are due to Mr. CURTIS C. HOWARD, of Columbus, and to Mr. PLINY BARTLETT, of Cincinnati, for material assistance rendered during the passage of the book through the press. If any errors are found which have escaped their very careful proof-reading, the author will be obliged to any one who will take the trouble to point them out.

COLUMBUS, OHIO,
April 1, 1878.

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CHEMISTRY.

CHAPTER I.

LAWS OF CHEMICAL COMBINATION.

1. Many common phenomena are the results of chemical action. If iron filings are moistened and exposed to the air, they become changed to the orange-red powder called iron rust. The iron loses its luster, its tenacity, its property of being attracted by a magnet; in fact, it loses its identity, and we recognize iron rust as a different kind of matter from iron. When a body is so altered that its physical properties disappear, and a new kind of matter has been formed, a chemical action has taken place.

The constituents of the atmosphere are continually acting upon the substances which are found on the surface of the earth, and are effecting in them chemical changes. Among these changes are the decay of leaves, the burning of wood and candles, the rusting of iron, and the souring of milk and cider. As the result of these actions new bodies are formed, which are essentially different from the original substances.

2. The atmosphere is so constantly engaged in producing chemical changes that we must first determine what its constituents are.

Experiment 1.—Place in a glass beaker a freezing mixture of ice and salt. After a little, the outside of the dish will be covered with moisture, which in process of time will collect in drops of water. See **Exp. 39.**

The atmosphere, therefore, contains water, which is usually disseminated through it as an invisible vapor. The quantity of aqueous vapor in the air is always small, and of no constant proportions. The average is 1.4 per cent.

The vapor of water may be removed from air and other gases by passing them through vessels containing calcium chloride or sulphuric acid or quicklime.

Exp. 2.—Expose a lump of quicklime in an open dish. After a few days it will crumble to a light powder. This is air-slaked lime. The lime has combined with the water in the air and has formed a compound which is called calcium hydrate.

After a longer exposure the lime will combine with another constituent of the air called carbonic acid, or carbonic anhydride, to form calcium carbonate. If old mortar be dropped in a dilute acid, it will *effervesce* or give off bubbles of the same gas, which has been obtained by long contact with the air. Carbonic anhydride forms usually four parts in 10000 of the atmosphere, but even this relatively small quantity is essential to the growth of plants.

Free carbonic anhydride may be removed from air or other gases by passing them through a solution of potassium hydrate, or through "milk of lime."

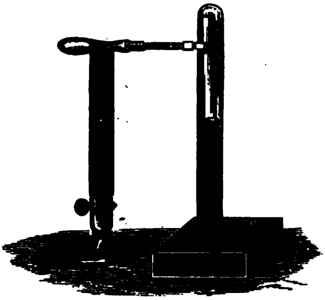

FIG. 1.

Exp. 3.—Invert a glass tube closed at one end and filled with dry air in a basin containing mercury. Wrap a piece of clean sodium in filter paper, and bring this within the tube. After a few hours the volume of the air will contract, and the mercury will rise and fill about one-fifth of the tube. Now, close the tube with the thumb, and remove it from the basin. Test the gas remaining by plunging an ignited splinter of pine within the tube. The blaze will instantly be extinguished.

The gas that remains, and that will not support combustion, is called *nitrogen.* It constitutes 79.19 per cent of dry air by volume.

The sodium has removed 20.81 per cent, by volume, of the air. This constituent of the air which supports combustion is called *oxygen.* Open the paper in which the sodium was wrapped. The metal will be seen to be coated with a dry powder, which is called sodium oxide (Na_2O). It has also gained in weight.*

Oxygen is the efficient agent in producing the changes mentioned in § 1. The nitrogen is inert, and its principal use seems to be to dilute the oxygen and diminish the rapidity of its action. When a metal corrodes or rusts in the air, it does so by combining with oxygen. The process is called *oxidation,* and the product formed by *oxidizing* a metal is called an *oxide* of that metal.

The air contains also very small traces of ammonia and other vapors, but these may be neglected for the present. All these constituents of the air are merely *mixed* together and are therefore readily separated. Water, for instance, will absorb from the air a greater proportion of oxygen than of nitrogen; so that the air which fishes breathe is richer in oxygen than that which we breathe.

The principal constituents of the atmosphere are water, carbonic anhydride, nitrogen, and oxygen.

3. We must also determine the constituents of water, because it is an efficient agent in producing chemical changes.

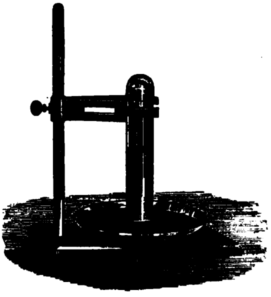

FIG. 2.

Exp. 4.—Fill a stout test tube with water and invert this in a dish of water. Pass into the mouth of the tube a small pellet of

---

*If the teacher has no mercurial cistern, he may remove the oxygen by phosphorus, or, better, by potassium pyrogallate (see **Exp. 78**).

sodium wrapped in filter paper. Bubbles of gas instantly rise to the top of the tube and force the water out. Remove the tube from the water, and apply a lighted splinter to its mouth. The gas burns with a pale flame.

This gas is called *hydrogen*, and constitutes $\frac{1}{9}$ of the weight of water. Test the water of the dish by reddened litmus paper; it will become blue. Moisten another litmus paper, and put a little of the sodium oxide, obtained by Exp. 3, on it; the same change of color will be produced, because sodium oxide has also been formed by the decomposition of the water.

Water, then, is composed of hydrogen and oxygen. When sodium oxide dissolves in water, it forms sodium hydrate, or the caustic soda of the apothecary (Na_2O, H_2O, or $2NaHO$).

Exp. 5.—Boil a few leaves of red cabbage in water, and decant the clear, purplish liquor. Caustic soda dropped in this infusion changes it to a green color.

Bodies which are capable of changing such vegetable blues to green are called, in ordinary language, *alkalies*. The common alkalies are soda, potassa, and ammonia. They have an acrid taste and a soapy feel.

Exp. 6.—Prepare chlorine water as directed in § **122.** A little of this dropped in the cabbage infusion, or on litmus paper, will instantly decolorize or bleach it.

Exp. 7.—Fill a flask completely with chlorine water, invert it in a cup of water, and expose it for some days to the sunlight. Bubbles of gas will collect in the upper part of the flask, and the odor of the chlorine will entirely disappear if it is exposed long enough.

Exp. 8.—Light a splinter of pine, and blow out the flame so as to leave only a glowing coal. Plunge this into the gas of the flask: it will instantly be re-lighted, and burn brightly.

This gas supports combustion, and is called *oxygen*. It constitutes $\frac{8}{9}$ of the weight of water. The chlorine has also decomposed the water; but, unlike sodium, it liberates oxygen and combines with the hydrogen. The compound formed is called hydrogen chloride, or, more frequently, hydrochloric acid (HCl).

Test the water in the cup with the cabbage infusion or with blue litmus paper. It will be reddened,* and the water will have a sour taste.

Bodies which change vegetable blues to red are called, in ordinary language, *acids*, because the common acids have a sour taste.

These experiments show that water contains oxygen and hydrogen. The following experiment shows that it contains only these gases.

Exp. 9.—Prepare hydrogen as directed in § **82**; dry it by passing the gas through a tube filled with calcium chloride, and attach to this a delivery tube drawn out to a fine orifice. After all the air has been expelled from the apparatus,† light the hydrogen, and hold over the flame a cold bell glass (Fig. 3). The hydrogen burns because it unites with the oxygen of the air, and the product of the combustion collects in drops on the inside of the bell glass. (See §§ 46 and 47).

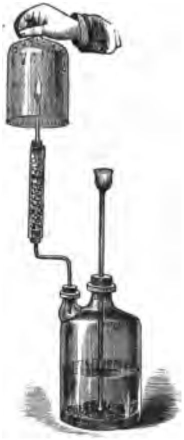

FIG. 3.

It is *water* (H_2O). Two parts, by weight, of hydrogen unite with sixteen parts, by weight, of oxygen to form eighteen parts of water. Thus, eight ounces of oxygen are required to burn one ounce of hydrogen to form nine ounces of water. These last quantities are evidently in the same proportions as those first given; or, $2 : 16 :: 1 : 8$.

These proportions are always the same. Because they are constant, and because the constituents can not be separated from each other by merely physical means, we say that water is a true chemical compound.

---

* If all the odor of the chlorine has not disappeared, it will also be more or less bleached.

† Hydrogen mixed with air is *dangerously explosive*.

The aqueous vapor in the atmosphere promotes many chemical changes: thus, iron and wood will remain unchanged for years in dry air; but in moist air, the iron readily rusts and the wood decays. The oxygen which causes the oxidizing of metals and the decay of vegetable matter is obtained by the decomposition of water.

4. **Chemistry** treats of the composition of bodies, and of those changes in matter by which the substances acted upon suffer a loss of identity.

The chemist endeavors to determine the composition of bodies by subjecting them to various experiments, which are designed to effect essential changes in their structure. By many such it has been found that a limited number of substances consist of a single uniform kind of matter — as, sodium, oxygen, hydrogen; and that by far the greater number of substances are composed of two or more constituents — as, water, sodium oxide, sodium hydrate.

5. Bodies which have been made to yield but one kind of matter are called *simple substances* or *elements.*

Bodies which may be separated into two or more elements are called *compound substances.*

The known elements are sixty-five in number. There can be no doubt that others will be discovered; and it is possible that some substances which are now considered simple will hereafter be found to be compound.

TABLE OF THE ELEMENTS.

I. THE NON-METALS — 13.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Fluorine	F	19.	Boron	B	11.
Chlorine	Cl	35.5			
Bromine	Br	80.	Carbon	C	12.
Iodine	I	127.	Silicon	Si	28.
Oxygen	O	16.	Nitrogen	N	14.
Sulphur	S	32.	Phosphorus	P	31.
Selenium	Se	79.4			
Tellurium	Te	128.			

II. The Semi-Metals — 13.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Vanadium	V	51.3	Titanium	Ti	50.
ARSENIC	As	75.	Zirconium	Zr	89.6
Niobium	Nb or Cb	94.	TIN	Sn	118.
Antimony	Sb	122.			
Tantalum	Ta	182.	Molybdenum	Mo	92.
Bismuth	Bi	210.	Tungsten	W	184.
			Uranium	U	120.

HYDROGEN —— H 1.

III. The Metals — 39.

Lithium	Li	7.	Cerium	Ce	92.
SODIUM	Na	23.	Lanthanum	La	92.8
POTASSIUM	K	39.1			
Rubidium	Rb	85.4	Thallium	Tl	203.6
Caesium	Cs	133.	LEAD	Pb	207.
			Thorium	Th	231.
SILVER	Ag	108.			
			Chromium	Cr	52.4
Glucinum	Gl or Be	9.4	Manganese	Mn	55.
MAGNESIUM	Mg	24.	IRON	Fe	56.
ZINC	Zn	65.	Cobalt	Co	59.
Cadmium	Cd	112.	Nickel	Ni	59.
CALCIUM	Ca	40.	GOLD	Au	197.
Strontium	Sr	87.5			
Barium	Ba	137.	Ruthenium	Ru	104.4
			Osmium	Os	199.2
COPPER	Cu	63.5			
MERCURY	Hg	200.	Palladium	Pd	106.6
			PLATINUM	Pt	197.4
ALUMINIUM	Al	27.5	Rhodium	Rh	104.4
Gallium	Ga	69.9	Iridium	Ir	198.
Indium	In	113.4			
Yttrium	Y	61.7	Davyum	Da	150?
Didymium	Di	96.			
Erbium	Er	112.6			

NOTE.—The atomic weights are those given in the "Neues Handwoerterbuch der Chemie." Other classifications are given on pp. 59, 60, 192.

The symbol placed after each element is the abbreviation of its Latin name; thus, H stands for hydrogen; Ag for silver (Argentum); Hg for mercury (Hydrargyrum); Fe for iron (Ferrum). These symbols are so convenient that the student should at once familiarize himself with those of the most common, the names of which in the table are printed in capitals.

6. The study of Chemistry is much facilitated by classifying the elements in groups, whose members have many characteristics in common. But it is impossible to draw any strict dividing line; and hence all such groupings must be regarded as made merely for the sake of convenience, and liable to be varied hereafter. It will be noticed that three principal groups are given: the non-metals, the semi-metals, and the metals. No definition has been given which sharply distinguishes them; but it may be generally observed, (1) That the metals are good conductors of heat and of electricity, and are characterized by a peculiar metallic luster; (2) The non-metals are non-conductors of heat and of electricity; (3) The metals are electro-positive elements, and the non-metals electro-negative. By this we mean that when their compounds are decomposed by the galvanic current, the metals tend to collect at the negative pole of the battery, and the non-metals at the electro-positive pole.* (4) Generally, the non-metals form, with oxygen, acid anhydrides, while the metals form basic anhydrides, as will be explained hereafter. (5) The semi-metals are elements which resemble the metals in their physical properties, and the non-metals in their chemical properties; that is, they have the luster of the metals, but their oxides are most frequently acid anhydrides.

7. The most important processes employed in chemistry are readily illustrated by a few experiments, which the student is earnestly requested to repeat for himself.

---

*See § 48.

I.—COMBINATION.

Exp. 10.—Cut off a thin slice of phosphorus, and, having dried it between two folds of filter paper, lay it on a dry plate. Now put upon this a flake of iodine. The two elements unite and evolve so much heat that a portion of the phosphorus combines also with the oxygen of the air, and burns brightly. White fumes are given off, which are a compound of phosphorus and oxygen, called phosphorus pentoxide. The red solid that remains on the plate is called phosphorus iodide.

Exp. 11.—Rub together in a mortar a small globule of mercury with a little more than five-fourths of its weight of iodine, moistened with a few drops of alcohol. The mercury and iodine unite to form a scarlet powder, which is called mercuric iodide.

Exp. 12.—Place a bright strip of zinc in a small dish, and cover it with water. Now drop on the zinc a few flakes of iodine. After a few hours the iodine will disappear in the liquid. It has united with a portion of the zinc to form zinc iodide. The combination may be accelerated by frequent stirring, and by gently warming the mixture.

If, now, the remaining zinc be removed, the zinc iodide may be obtained by evaporating the liquid on a water bath.

Exp. 13.—Prepare a strong solution of chlorine water, as directed in § **122.** Put some of this in a glass vial, with a very small globule of mercury, and shake frequently. After a time the mercury will disappear, and most of the odor of the chlorine; the chlorine will unite with the mercury to form mercuric chloride.

This body may be obtained by evaporating the liquid, or the solution may be used in the experiments which follow.

8. These experiments show that two bodies may combine directly.

The process of uniting two bodies to form a chemical compound is called *synthesis.* When only two elements enter into combination, the product is called a *binary* compound. Such compounds are named by affixing the termination *ide* to the non-metallic, or electro-negative, element, and prefixing the name of the metal, or the electro-positive element; as, zinc iodide, mercuric iodide.

In this way we may name the oxides, chlorides, iodides, phosphides, etc.; but it is important to note that the termination *ide* is never used except with binary compounds.

9. The foregoing experiments show that chemical changes are marked by alterations in color, taste, odor, form, and sometimes by the development of heat and light. The compounds formed are essentially different from the elements that enter into combination. On the other hand, if bodies are merely mixed together, no such changes occur.

Exp. 14.—Rub together in a mortar 56 parts of iron filings and 32 of sulphur. Divide the mixture into four equal portions. From the first portion the iron may be removed by a magnet; from the second portion the sulphur may be removed by dissolving it in carbonic disulphide; and from the third, by directing upon it a gentle stream of water, which will suffice to wash away the lighter particles of the sulphur, and leave the heavier iron behind. Now heat the fourth portion in a test tube. The sulphur and iron combine to form ferrous sulphide, which is a true chemical compound whose constituents are inseparable by mechanical means.

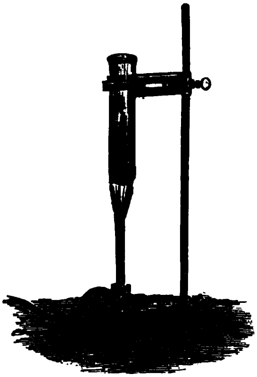

FIG. 4.

Further, a mixture may be made in all conceivable proportions. This is not the case in a chemical combination. In Exp. 12, a portion of the zinc was not acted upon. If in Exp. 11 we employ too much iodine, the excess will remain uncombined and mixed with the mercuric iodide. In the last example, if an excess of sulphur is used, it may be dissolved by carbonic disulphide, after first pulverizing the product.

10. Law of constant proportions.—*In every chemical compound, the proportions of the elements united are always fixed, definite, and invariable.*

Thus the following named binary compounds are always found to contain:

Sodium chloride,	23	parts of	sodium,	35.5	parts of	chlorine.
Sodium iodide,	23	"	sodium,	127	"	iodine.
Potassium chloride,	39	"	potassium,	35.5	"	chlorine.
Potassium iodide,	39	"	potassium,	127	"	iodine.
Zinc iodide,	65	"	zinc,	254	"	iodine.
Zinc chloride,	65	"	zinc,	71	"	chlorine.

These are the only binary compounds of iodine and chlorine with sodium, potassium, and zinc. Iodine and chlorine, however, combine with some of the elements to form two or more distinct compounds; but for the same compound, the proportions are always constant.

Exp. 15.—Repeat Exp. 11, using only five-eighths as much iodine as mercury. A greenish-yellow powder will be produced, containing twice the proportional quantity of mercury. It is called mercurous iodide (HgI, or Hg_2I_2).

If a quantity of iodine intermediate between five-fourths and five-eighths its weight of mercury be used, both iodides will be produced and remain mixed together. Strong alcohol will dissolve out of the mixture the mercuric iodide, and leave the mercurous iodide behind.

Mercury, therefore, forms two compounds with iodine: 200 parts of mercury may combine with 127 parts of iodine to form mercurous iodide, or with 254 parts of iodine to form mercuric iodide. The proportion of iodine in the second is exactly twice that of the first. We distinguish between two such compounds by the terminations *ic* and *ous* added to the more positive element: the *ic* denoting the higher degree of combination; the *ous*, the lower.

Exp. 16.—Boil a solution of mercuric chloride with a globule of metallic mercury. A white powder will separate from the mixture. This is mercurous chloride ($HgCl$, or Hg_2Cl_2).

The proportion of chlorine in the mercuric chloride is twice that in the mercurous chloride. Some such simple relation is generally found when two elements form more than one compound. Hence:

11. The Law of multiple proportions.—*When one body is capable of uniting with another body in several proportions, these proportions bear a simple relation to each other.*

Thus, an element, A, may unite with another element, B, to form compounds, which may be represented by

$$A + B,\ A + 2B,\ A + 3B,\ A + 4B,\ A + 5B,$$
$$2A + 3B,\ 2A + 5B,\ 2A + 7B, \text{ etc., etc.}$$

We have an excellent illustration of this law in the compounds of nitrogen and oxygen. These are five in number:

	PARTS IN 100 BY WEIGHT.				RATIOS.			
	N.		O.		N.		O.	SYMBOLS.
Nitrous oxide,	63.64	:	36.36	::	28	:	16	N_2O
Nitric oxide,	46.67	:	53.33	::	28	:	32	N_2O_2
Nitrous anhydride,	36.85	:	63.15	::	28	:	48	N_2O_3
Nitric peroxide,	30.44	:	69.56	::	28	:	64	N_2O_4
Nitric anhydride,	25.93	:	74.07	::	28	:	80	N_2O_5

This shows that 28 parts of nitrogen may combine to form a series of compounds with oxygen, containing one, two, three, four, and five times 16 parts of oxygen. When a series of two or more binary compounds are formed of two elements, we may distinguish between them by the prefixes *mono* or *prot* = one; *bi*, *deut*, or *di* = two; *tri* or *ter* = three; *tetra* = four; *penta* = five, etc., affixed to the element that increases by multiples. Sometimes, also, the names of the elements are separated by *of:* thus the last series may be severally named protoxide, dioxide, trioxide, tetroxide, and pentoxide of nitrogen.

Many compounds have two or more names: one the vulgar name, others derived from former theories of chemists, and still others in modern use. Thus the two chlorides of mercury have each a half a dozen names, the following of which are still allowable:

Formula,	Hg_2Cl_2, or HgCl.	$HgCl_2$.
Vulgar name,	Calomel.	Corrosive Sublimate.
Old name,	Protochloride of Mercury.	Bichloride of Mercury.
New name,	Mercurous Chloride.	Mercuric Chloride.

12. It follows naturally, from the laws of constant and multiple proportions, that the weights in which bodies unite may be represented by numbers. We also find that the same number, or a multiple of it, will represent the proportion, by weight, in which any element will combine with any other element. Thus iodine may always be represented by 127, or by some multiple of it. The numbers thus found are called the *combining numbers* of the elements.

Law of combining proportions.—*Every element in combining with other elements does so in a fixed proportion, which may be represented numerically.*

The numbers given on pp. 12 and 13 are the combining proportions in which each element unites with the other elements. Further, it has been agreed that each symbol shall not only be an abbreviation of the name of an element, but also represent one combining number. Hg, therefore, represents 200 parts of mercury by weight; I, 127 parts of iodine; O, 16 parts of oxygen, etc. A number placed below a symbol represents how many multiples of the element are taken: thus, I_2 represents two combining proportions, or 254 parts, of iodine. We may then represent mercurous iodide by HgI, or by Hg_2I_2, and mercuric iodide by HgI_2. If we desire to represent a multiple of a compound, we do so by placing a numeral before the symbol of the compound; thus,

$2Hg_2I_2$ represents two proportions of mercurous iodide, $2HgI_2$, two proportions of mercuric iodide. The number, when placed before a compound, multiplies each element in the compound by itself. The same thing is sometimes done more conveniently by inclosing the symbols within parentheses, and placing the numeral either before or below the parenthetical marks; for example, $2HgI_2$, $2(HgI_2)$, $(HgI_2)_2$, represent the same quantities.

13. **Binary compounds may also unite** and produce other compounds.

Exp. 17.—Quicklime (CaO) and water (H_2O) are binary compounds. Put a large lump of quicklime on a plate, and pour on it a small quantity of water. The two binaries unite; the lime becomes heated and crumbles away to a light powder, which is called slaked lime. Its composition may be represented by CaO, H_2O, or CaH_2O_2, or $Ca(OH)_2$.

Exp. 18.—Place a piece of clean sodium in a bottle filled with dry air or oxygen. The sodium changes to sodium oxide (Na_2O). Now bring into the flask a stream of carbonic anhydride (CO_2).* The two binary compounds unite to form sodium carbonate (Na_2O, CO_2, or Na_2CO_3).

When two binary compounds unite, the product contains three elements, and is called a *ternary* compound. Thus, sodium carbonate contains three elements, Na, C, and O.

A few compounds are formed by the union of two ternaries. These usually contain four elements, and are called *double salts*. Common alum is an example: it consists of potassium sulphate and aluminium sulphate; besides which it contains water, which is called water of crystallization. The entire formula of alum is $K_2O, SO_3 + Al_2O_3, 3SO_3 + 24H_2O$, or $KAl2SO_4 + 12H_2O$.

14. **Compounds may also be formed indirectly.**

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* The directions for the preparation of this are on page 171.

II.—SUBSTITUTION.

Exp. 19.—Put a little mercuric iodide in a vial half filled with water. Add a few drops of saturated chlorine water, and shake the mixture. A part of the iodine is set free and darkens the liquid. The mercury is not seen, because it has combined with the chlorine to form mercuric chloride, and is dissolved. The odor of the chlorine also disappears.

The whole of the iodine may be displaced by the chlorine, by adding the chlorine water in small quantities, and shaking the mixture after each addition. The free iodine may be separated from the mixture by adding a teaspoonful of chloroform to the water, and shaking. The chloroform dissolves the iodine and settles to the bottom. The supernatant liquid may then be poured off, and the mercuric chloride be obtained by evaporation.

Exp. 20.—Mercurous iodide, treated in the same way, yields mercurous chloride and free iodine.

Exp. 21.—Put another portion of mercuric iodide in a small beaker with a little water. Place in this a clean zinc strip, and warm gently. In a few hours the mercuric iodide will entirely disappear, and a coating of mercury will be seen on the zinc. In this case the zinc has displaced the mercury in the compound, and has formed zinc iodide, which remains in the solution. It may also be obtained by filtering and evaporating the liquid.

15. These experiments show that we may form new compounds by displacing one element by another. The process of forming a new compound by displacement is called *substitution.*

III.—METATHESIS.

Exp. 22.—Pour into a test tube a solution of mercuric chloride, and add to this, drop by drop, a solution of zinc iodide. The elements of the two compounds will be rearranged to form two new compounds,—solid, red, mercuric iodide and zinc chloride.*

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*The student will notice that the red powder, which is at first formed, immediately disappears, because an *excess* of mercuric chloride dissolves it: that it then settles to the bottom of the tube, or *precipitates;* and, finally, if more zinc iodide is added, and the mixture shaken, it again disappears, because an *excess* of zinc iodide dissolves it. The example shows the importance of avoiding excess in chemical manipulations. A drop too much is *excess.*

If the mercuric iodide be filtered off, the zinc chloride, which remains dissolved, may be obtained by evaporating the solution to dryness.

Exp. 23.—Provide a small flask, as shown in Fig. 5, with a cork through which passes a long funnel tube, A, reaching nearly to the bottom of the flask; also a shorter tube, B, bent at right angles, and just passing through the cork. Make all the fittings air-tight. Now put some ferrous sulphide in the flask, and insert the cork. Pour through the funnel tube a little hydrochloric acid. Chemical action will immediately begin, and an extremely offensive gas, hydrogen sulphide, will be given off.

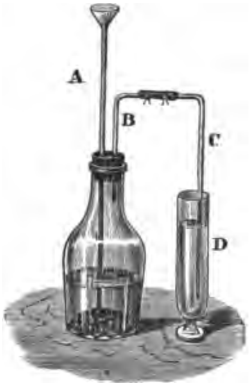

FIG. 5.

Hydrochloric acid is a solution of hydrogen chloride. When this is poured on ferrous sulphide, the elements are arranged into two new compounds, — ferrous chloride and hydrogen sulphide.

Exp. 24.—Having previously attached, by a rubber tube, the glass tube, C, to the flask, pass the escaping hydrogen sulphide into any of the compounds of mercury previously obtained. They will all blacken from the formation of mercurous sulphide, or mercuric sulphide, and the hydrogen will enter into combination with the iodine or with the chlorine.

16. These experiments show that new compounds may be formed by an interchange of the elements previously existing in other compounds.

The process of forming new bodies by an interchange of the elements of two compounds is called *double decomposition*, or *metathesis*.

17. Chemical changes like those already described are called *reactions;* the bodies which take part in them are called *reagents*. We may represent reactions by equations not unlike those of algebra. The sign $+$ represents *added to*, or *and;* the sign —, *taken from;* the sign =, *produces*, or *results in*. Thus, the formula,

$$\mathrm{Hg\,Cl_2} + \mathrm{Zn\,I_2} = \mathrm{Hg\,I_2} + \mathrm{Zn\,Cl_2}$$

means "zinc iodide *added to* mercuric chloride, *produces* mercuric iodide and zinc chloride." The formula is never correct unless the sum of the combining numbers on one side of the sign of equality is exactly equal to the sum on the other.

$$\begin{array}{ccccccc} \mathrm{Hg\,Cl_2} & + & \mathrm{Zn\,I_2} & = & \mathrm{Hg\,I_2} & + & \mathrm{Zn\,Cl_2} \\ \underbrace{200+71}_{271} & + & \underbrace{65+254}_{319} & = & \underbrace{200+254}_{454} & + & \underbrace{65+71}_{136} = 590 \end{array}$$

Further, if we have given the left-hand side of the equation, and one product, we can predict, in many cases, what the other product will be. It will generally be a combination of the elements not used to form the product given.

In this book, the sign ⌃ placed over a symbol indicates that a gas is evolved; the sign ⌄ placed beneath, that a solid is formed and precipitates.

Having by some one of these methods obtained a new compound, the chemist endeavors to confirm the conclusions he has reached respecting the composition of the body, by again separating it into its elements.

IV.—ANALYSIS.

18. **The process of separating** a compound into its constituents is called *analysis*.

Exp. 25.—Place a gramme of mercuric oxide in a tube of hard glass, and heat strongly. It will be decomposed into mercury and oxygen. The former will collect in metallic globules on the colder portions of the tube, and the latter will escape as a gas. The presence of oxygen in the tube may be tested by first lighting a splinter of pine, then blowing it out so as to leave a glowing coal.

and introducing this into the tube. If oxygen is present, the coal will burst into a flame. The oxygen may be collected by previously connecting to the glass tube, by means of a perforated cork, a delivery tube which dips under water in a pneumatic cistern, as in Fig. 6. A cylinder filled with water is then inverted over the mouth of the delivery tube. As fast as the gas is evolved, it rises into the cylinder, and is there collected.

Every 216 parts, by weight, of the red oxide yields 200 parts of mercury and 16 of oxygen, also by weight.

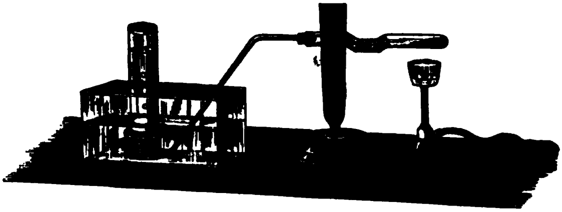

FIG. 6.

Exp. 26.—Heat iodic anhydride in apparatus similar to that shown in Fig. 6. It separates into oxygen and iodine. The iodine at first fills the tube with a purple vapor, which soon condenses in grayish-black flakes. The oxygen may be collected and examined as before.

Every 334 parts, by weight, of iodic acid yields 254 parts of iodine and 80 of oxygen.

Exp. 27.—Heat dry mercuric iodide in a dry test tube. It does not decompose, but is changed to vapor, which condenses in yellow crystals near the top of the tube. This is called *sublimation.* If some of these yellow crystals are shaken out upon paper and rubbed with a knife-blade, they become red; heated again upon the paper, they become yellow; again rubbed, red; and so on. No chemical change, however, has taken place.

19. Mere change of temperature will not suffice for the analysis of this body. We may, however, determine its composition indirectly. Thus, by making such weighings as are necessary, we may ascertain, in Exp. 19, that every 454 parts of mercuric iodide yields 254 parts of iodine; by Exp. 21, that the same quantity yields 200 parts of mercury. Also, by Exp. 22, that to form 454 parts of mercuric iodide requires 271 parts of mercuric chloride and 319 parts of zinc iodide; and, by similar experiments, learn that 271 parts of mercuric chloride contain exactly 200 parts of mercury, and that 319 parts of zinc iodide contain exactly 254 parts of iodine. Finally, we may determine, by Exp. 11, that the exact proportions required to form mercuric iodide are 200 parts of mercury and 254 parts of iodine. Since all these agree, we are certain that the result is correct.

20. When reagents are employed to determine *what* elements are present in a body, the process is called *qualitative analysis.* When reagents are employed to determine *how much* of an element is present in a body, the process is called *quantitative analysis.*

21. We have learned by these experiments that different substances combine *with different degrees of energy.* Phosphorus and iodine unite as soon as they are brought in contact. Mercury and iodine require to be triturated, or rubbed together; but, once united, the compound is not decomposed by heat. On the other hand, the red oxide of mercury may be formed by prolonged heating of mercury in the air, at a temperature of about 315° C., and is again decomposed into its constituents at a dull red heat.

We have also learned that the same matter may successively form a part of several different compounds. With sufficient care in experimenting, we can follow the same matter through a dozen changes without losing a particle. *No matter is destroyed* by chemical changes, however many they are, or however violent they may appear.

Recapitulation.

All substances are either simple or compound, or are mixtures.

Simple substances are . . .
- electro-negative
  - non-metals, 13.
  - semi-metals, 13.
- electro-positive — metals, 39.

Compound substances contain
- two elements — binary.
- three elements — ternary.
- four elements — double salts.

In binary compounds —
The negative element takes the termination *ide*.
It may take the prefix *mono*, *di*, *tri*, *tetra*, or *penta*.
The positive element may take the termination *ous* or *ic*.

Chemical changes are produced —

By the union of two bodies	Combination.
By displacing one element by another	Substitution.
By an interchange of elements	Metathesis.
By the decomposition of bodies	Analysis.

Analysis is either Qualitative or Quantitative.

The laws of combination are —
The law of constant proportions.
The law of multiple proportions.
The law of combining proportions.

CHAPTER II.

CHARACTERISTICS OF CHEMICAL AFFINITY.

22. Few of the elements exist, as such, free in nature. Gold, platinum, copper, mercury, silver, sulphur, and carbon are found native, but most of the others have been obtained only from their compounds. The unstratified portion of the earth's crust, which is considered to be the source from which the other rocks are formed, consists mainly of the compounds of eight elements, although it contains traces of many others.

The principal constituents of the primary rocks are given in the following table, together with the weights of each, reckoned on a scale of 100 parts.

Oxygen,	46.	Aluminium,	8.	Calcium,	3.5.	Potassium,	2.4.
Silicon,	30.	Iron,	6.	Sodium,	2.5.	Magnesium,	1.4.

We find in the stratified rocks minerals containing comparatively large quantities of carbon, sulphur, arsenic, and chlorine. The metals—copper, lead, zinc, and tin—are somewhat abundant, although their ores are sparsely distributed in mineral veins.

23. The waters of the earth are composed of hydrogen and oxygen, but contain in solution notable quantities of sodium chloride and other salts.

The atmosphere is a mixture of nitrogen, oxygen, and small amounts of carbonic anhydride and aqueous vapor.

Small quantities of phosphorus are found in plants and animals.

The nineteen elements named are the only ones which are found in great abundance. The greater portion of the remaining elements are seldom met with, and some of these are so rare that they have been handled by but few chemists.

24. The force which holds like particles of matter together is called *cohesion.* It is strongly exerted in solids, feebly in liquids, and appears to be entirely absent in gases. The energy of cohesion is dependent: (1) on the kind of matter; thus, it is evident that the particles of iron cohere with greater energy than those of lead, because it requires a greater force to pull them apart: (2) on the temperature; water, a liquid at ordinary temperatures, changes in the cold of winter to solid ice, and, on boiling, passes away in aëriform steam: (3) fluids are greatly influenced by pressure; thus, if ether, a liquid, under the pressure of one atmosphere, be introduced into the vacuum at the top of a barometer tube, it instantly changes to vapor. (See Norton's Nat. Philos., Art. 569). The cohesion of any substance is, therefore, only relative.

25. Fifty-eight elements are, at ordinary temperatures, solids; but even refractory solids, like copper, silver, and gold, have been melted and volatilized. Mercury and bromine, the only elements which are ordinarily liquid, easily vaporize and are as easily solidified by comparatively slight changes in temperature. Under the joint influence of cold and pressure, chlorine, a gaseous element, becomes liquid; and some compound gases, like ammonia and carbonic anhydride, become not only liquid, but solid.

Gases like these are called *coercible gases.*[*] The resources of experiment have lately availed to condense oxygen, nitrogen, and hydrogen. These elements, however, from the difficulty experienced in condensing them, are frequently spoken of as the *permanent gases.* It is probable that any one of the elements may be obtained in either the solid, liquid, or aëriform condition. This statement is also true of many compounds; but a large

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[*] The following gases are condensed to liquids at a temperature of 0° C., under the atmospheric pressures named below:

		PRESSURE IN ATMOSPHERES.			PRESSURE IN ATMOSPHERES.
Sulphurous anhydride,	SO_2	1.53	Sulphuretted hydrogen,	H_2S	10.
Cyanogen,	CN	2.37	Hydrochloric acid gas,	HCl	26.20
Ammonia,	NH_3	4.40	Nitrous oxide,	N_2O	32.20
Chlorine,	Cl	6.	Carbonic anhydride,	CO_2	38.50

The following bodies have been condensed to liquids under a pressure of one atmosphere, at the temperatures given below:

Carbonic anhydride,	— 78° C.	Bromine,	+ 63° C.
Chlorine,	— 35°	Water,	+ 100°
Cyanogen,	— 21°	Iodine,	+ 200°
Sulphurous anhydride,	— 10°	Mercury,	+ 350°

In condensing gases it is usual to employ conjointly, when possible, the effect of cold and of pressure. O is condensed at — 140° under a pressure of 320 atmospheres; N, at + 13°, and under 200 atmospheres. When H was allowed to expand suddenly from a pressure of 280 atmospheres, it apparently formed solid particles described as "hail." The cold produced by the sudden expansion must have been very great.

number of these bodies, of which marble and wood are examples, are so readily decomposed by heat, that we can not hope to volatilize them.

It is well to remark that in chemistry no distinction is drawn between gases and vapors.

26. The force which unites unlike particles of matter, and keeps them in combination, is called *affinity.* It acts between different substances with a different amount of energy, and is modified by the other molecular forces. Although most of the experiments in this book illustrate the characteristics of chemical affinity, the following examples are given to familiarize the student with some of the most important.

27. Affinity varies with the kind of matter. Iodine readily unites with the metals, but all metallic iodides are decomposed by free chlorine, showing that the affinity of chlorine for metals is stronger than that of iodine. Nevertheless, iodine has a stronger affinity for oxygen than chlorine has.

Exp. 28.—Add weak chlorine water to a solution of potassium iodide, to which some boiled starch has been added. The blue color which is produced shows the presence of free iodine.*

28. It is influenced by the mass or the excess of one substance. Sulphuric acid has generally a stronger affinity for metallic oxides than hydrochloric acid; but if to a solution of blue sulphate of copper a large amount of hydrochloric acid be added, the solution will change to a green color. This shows that cupric chloride has been formed, although, at the same time, sulphuric acid must have been set free. The result must be attributed to the excess in quantity of the hydrochloric acid.

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* $KI + Cl = KCl + \underbrace{I}$.

Exp. 29.—Fill a hard glass tube with iron turnings; place this in a furnace and heat to redness. (Fig. 7). Now pass through the tube a current of steam. The water will be decomposed; its oxygen unites with the iron to form an oxide of iron; hydrogen is liberated, and may be collected at the other end of the tube.*

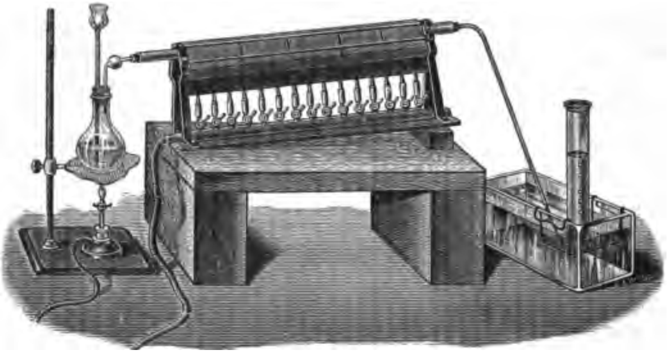

FIG. 7.

Exp. 30.—When the iron is well oxidized, replace the steam by a current of dry hydrogen: the operation is reversed. The oxide of iron is reduced to metallic iron, and steam passes out of the other end of the tube, or collects as drops of water in the colder portions.†

In the first instance, the iron is enveloped by steam, and the hydrogen is at once removed from the sphere of action. In the second instance, the hydrogen is in greater quantity, and the steam formed is prevented from acting upon the iron.

29. **The same element** does not exhibit the same energy under all circumstances. Thus, if hydrogen be passed into water which contains iodine in suspension, no action will take place. Neither does iodine decompose water to unite with its hydrogen. If, however, iodine is placed in water, together with some other substance that is ca-

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* $4\ H_2O + 3\ Fe = Fe_3O_4 + 4\ H_2$.

† $4\ H_2 + Fe_3O_4 = 4\ H_2O + 3\ Fe$.

pable of uniting with the oxygen of the water, it readily unites with the hydrogen that is liberated.

Exp. 31.—Add a few flakes of iodine to a solution of potassium iodide. They will dissolve, on stirring, to form a blood-red liquid. Now add this, drop by drop, to a *very dilute* solution of sulphurous acid or of sodium hyposulphite, previously mixed with a very little boiled starch. The sulphurous acid changes to sulphuric acid by uniting with the oxygen of the water.* Hydrogen is liberated, and, at the same instant, unites with the iodine to form hydriodic acid.† So long as free iodine is present, it will be manifested by changing the starch blue; but this color will disappear when all the iodine is converted to hydriodic acid.

In this experiment the hydrogen is said to be in the *nascent* state; that is, in the state of being liberated. All bodies in this state have much stronger affinities than when they are used in an isolated form.

Affinity is also influenced by the state of division of matter.

Exp. 32.—Dissolve a few small pieces of phosphorus in carbonic disulphide. Dip a feather into this solution and then draw it quickly over dry paper. The carbonic disulphide soon evaporates and leaves the phosphorus in a finely divided state on the paper. This exposes so much surface to the action of the air, that the phosphorus and oxygen combine rapidly and burst into a flame.

Exp. 33.—Put some alcohol in a saucer and set it on fire. Gunpowder may be dropped through the flame without igniting. If, however, fine iron filings be dropped into the flame, they will burn with bright scintillations. (See **Exp. 194**).

30. Affinity, like cohesion and adhesion, increases with the extent of surface exposed to its action, and is, therefore, generally the more energetic the more finely pulverized the bodies are which are acted upon. An apparent exception to this is found in the fact that a heap of charcoal dust will burn less readily than one of lump charcoal. This is easily explained; for the lump charcoal permits the air to circulate freely between its interstices, and thereby exposes a larger surface than the charcoal dust, which can be enkindled only on the outside of the heap.

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* $H_2O + H_2SO_3 = H_2SO_4 + H_2$.

† $H_2 + I_2 = 2HI$; or together, $H_2O + H_2SO_3 + I_2 = H_2SO_4 + 2HI$.

31. Affinity varies with the state of cohesion. Chemical affinity acts only at insensible distances. The more points of contact, the more readily will bodies unite. Any thing that tends to overcome the cohesion of a body tends also to augment its affinity for other bodies. Generally speaking, two solids can not be made to unite by pulverizing them together; the principal exceptions being those cases in which a liquid is set free by the reaction.

Exp. 34.—Rub together in a mortar crystals of oxalic acid and caustic lime. The two may be made to unite, because, at the beginning of the action, a little of the water of crystallization of the acid is set free, and acts as a solvent.

Exp. 34. (*a*)—Rub together 5 parts of KI and 4 parts of $HgCl_2$. They will combine to form red HgI_2 and KCl. This is a marked exception.

Exp. 35.—Rub together oxalic acid and sodium carbonate. No apparent action takes place; but, if a little water be added, the two unite with a rapid evolution of carbonic anhydride.

32. It is a general principle that to produce combination, at least one of the bodies must be in the fluid state. We have seen that the cohesion of solids is overcome by heat liquefying or vaporizing them. It may also be overcome by the adhesion of liquid particles, producing what is termed a *solution.*

Exp. 36.—Pulverize 20 grammes of common alum; place it in a flask, and pour over this 50 grammes of cold water. The whole of the alum will not dissolve, even after repeated stirring. Now heat the flask, and all will dissolve. The solution has a sweet and astringent taste.

Exp. 37.—Set the solution away to cool: small, octahedral crystals are speedily formed (see Fig. 8); and, if the liquid is cooled to the freezing point, nearly all the alum will crystallize out.

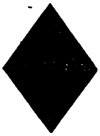

FIG. 8.

Such simple solutions can not be regarded as due to chemical reactions; for, excepting the mere liquefying of the solid, no change has been produced in its properties.

When a solution contains as much solid matter as it is capable of dissolving at any given temperature, it is said to be *saturated.* Common salt is about equally soluble at all temperatures. Some bodies are more soluble at a particular temperature than either above or below it. Thus, the solubility of sodium sulphate increases from 0° C. to 33° C., and then diminishes; but the solubility of most bodies is increased by an elevation of temperature. Marked exceptions are found in some lime compounds.

Exp. 38.—Put a tablespoonful of slaked lime into a pint flask; fill with water, and shake the flask for some time vigorously. Now let it stand undisturbed until the excess of lime has entirely settled to the bottom. Then pour a little of the supernatant fluid into a test tube and heat. It will soon become cloudy, showing that hot water is not as good a solvent for caustic lime as cold water.

33. Simple solutions are generally attended by the absorption of heat, due to the passage of the solid to the liquid condition.

Exp. 39.—Mix two pounds of snow with one pound of common salt. Both will partially dissolve, and a "freezing mixture" will be produced capable of congealing water. A pleasing way of showing this is to select two test tubes of not quite the same size, and, having put a little water in the larger, place the smaller within it. By stirring the mixture with this apparatus, a little cup of ice will be formed between the tubes.

34. There are two kinds of solutions: (1) the *simple solutions*, which have already been described, and (2) *chemical solutions*, in which the body first enters into a new chemical compound, which is then dissolved. In chemical solutions, although heat facilitates the formation of the solution, the *quantity* of the body dissolved is always dependent on the quantity of the solvent present; because the proportions in which bodies combine are invariable, and are not affected by differences in temperature. So, also, a chemical solution generally liberates heat.

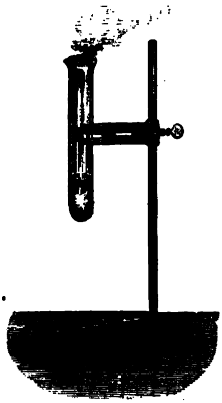

FIG. 9.

Exp. 40.—Place a teaspoonful of copper filings in a test tube, and cover them with strong nitric acid (Fig. 9). Copious red fumes will be given off, the tube will become warm, and, if enough acid be added, all the copper will disappear in the liquid. If this be evaporated, crystals of cupric nitrate may be obtained.*

The liquids used to produce chemical solutions are generally acids. In some cases, aqueous solutions of the alkalies, or of the alkaline sulphides, are employed.

35. The solvents suitable in any given case, either for simple or chemical solutions, are to be learned only in detail. Water is the best solvent for compounds of the metals; alcohol and ether are good solvents for most organic compounds; chloroform and carbonic disulphide dissolve iodine and phosphorus.

The solvent powers of liquids have a wide range. Water dissolves all normal nitrates and chlorates; all chlorides except those of silver, lead, thallium, and the cuprous and mercurous chlorides; and most sulphates—those of barium, strontium, lime, and lead being prominent exceptions. Some bodies, like calcium chloride and zinc chloride, are so soluble that, if placed in an open vessel, they attract enough water from the air to form a solution. Such bodies are called *deliquescent*.

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* $3Cu. + 4(H_2O,\ N_2O_3) + air = 3(CuO,\ N_2O_5) + 4H_2O + N_2O_4$.

36. Liquids also dissolve one another: alcohol and water, in all proportions; ether and water, in proportions of about one-tenth of each. Benzine dissolves many oils, and very many of the oils are good solvents for each other.

Solutions of gases are made by passing the gas into cold water or other liquids.* Gases are generally absorbed more abundantly by cold water than by warm water. If a solution of gases be warmed, some of the gas is driven off, and at the boiling temperature, all of the gas is expelled. Boiled or distilled water tastes "flat," because of the absence of the gases usually found in well water. The gases also escape when the solutions which contain them are frozen; that is, when the water becomes solid.

If the temperature remains unchanged, it is also true, within certain limits, that the weight of a gas absorbed by water increases with the pressure. The volume of the gas absorbed remains the same, because the pressure to which it is subjected condenses it.

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* The following table shows how many volumes of the gases named are absorbed by one volume of water and of alcohol, under the pressure of one atmosphere, or at 760 mm. Barometer.

COËFFICIENT OF ABSORPTION.

		WATER.		ALCOHOL.	
		At 0° C.	At 10° C.	At 0° C.	At 10° C.
Hydrogen,	H	0.0193	0.0193	0.02569	0.06786
Nitrogen,	N	0.02035	0.01607	0.12634	0.12276
Oxygen,	O	0.04114	0.03250	0.28397	0.28397
Atmospheric air,		0.0247	0.01953		
Carbonic anhydride,	CO_2	1.7967	1.1847	4.3295	3.5140
Hydrogen sulphide,	H_2S	4.3706	3.5838	17.891	11.9922
Sulphurous anhydride,	SO_2	78.789	56.647	328.62	190.21
Hydrochloric acid,	HCl	500.	418.		
Ammonia,	NH_3	1050.	813.		

Thus, water at 15° C. takes up its own bulk of carbonic anhydride, or about $\frac{1}{500}$ part of its weight. Under pressure of two atmospheres, it absorbs $\frac{1}{250}$ of its weight; of four atmospheres, $\frac{1}{125}$ of its weight, etc. The "soda water" of the confectioner is water charged with carbonic anhydride under pressure. When the pressure is removed, the greater part of the gas escapes with effervescence, because the gas resumes its former volume.

37. When two bodies have a tendency to react upon each other, the affinity between them is greatly modified by the natural cohesion of the product.

Berthollet's first law: *Solutions of two compounds can not be mixed together without a double decomposition taking place, if any two of the constituents can form an insoluble compound.*

We have already had an example that corroborates this, in Exp. 20. Mercuric chloride is soluble, and mercuric iodide is insoluble, in water; hence, if mercuric chloride is mixed with any solution containing a soluble iodide, mercuric iodide will be formed, although we know, by Exp. 19, that the affinity of mercury for free chlorine is stronger than for free iodine.

Exp. 41.—Mix a solution of mercuric chloride with a solution of potassium iodide. Mercuric iodide will be separated. The experiment may be repeated with sodium iodide or zinc iodide.

38. The formation of a solid insoluble in the liquids mixed together is called *precipitation.* The solid which separates is called a *precipitate.*

Exp. 42.—Make an alcoholic solution of potassium acetate, and pass into this a stream of carbonic anhydride: potassium carbonate will precipitate, because it is insoluble in alcohol, and acetic acid will be set free.

Exp. 43.—Add acetic acid to an aqueous solution of potassium carbonate. The reaction will be reversed: viz., potassium acetate will be formed, and carbonic anhydride will be set free as a gas.

We may explain the last reaction thus: (1) the acetic acid has a stronger affinity for potassium than carbonic anhydride; or (2) carbonic anhydride is but slightly soluble in water, and is, besides, naturally an aëriform body.

39. The volatility of the product certainly influences affinity. Thus, limestone or calcium carbonate, when strongly heated, breaks up into calcium oxide and carbonic anhydride.

Berthollet's second law: *If any two bodies whose constituents are capable of interchanging and forming a volatile product are heated together, these constituents will unite and volatilize.*

Exp. 44.—Add to a solution of calcium chloride a solution of ammonium carbonate. Calcium carbonate will precipitate, and ammonium chloride remain dissolved in the liquid.*

Exp. 45.—Heat together an intimate mixture of powdered calcium carbonate and ammonium chloride. At a temperature a little above 100° C., calcium chloride and ammonium carbonate will be formed: the latter is volatile and escapes.†

The reaction in Exp. 42 is explained by the first law—an insoluble precipitate is formed: the reaction in Exp. 43, by the second law—a volatile product is formed.

40. Affinity is in some cases influenced by *adhesion.*

Exp. 46.—Platinum sponge affords such an extent of surface to the air, that a small piece contains a large quantity of absorbed oxygen. If the dried sponge be brought near a current of dry hydrogen, the two gases are brought so close together that they unite, and the hydrogen is enkindled.

Instances are known of greasy rags, heaped together, taking fire spontaneously within twenty-four hours. The spontaneous combustion of porous bodies like cotton or sawdust saturated with oil is not infrequent, and is due to a similar cause. These bodies condense the air within their pores; oxidation commences and liberates a small quantity of heat; this accelerates the oxidation, and thus the process goes on with increasing rapidity until the mass bursts into a flame.

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* $CaCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + \underset{\downarrow}{CaCO_3}$.

† $CaCO_3 + 2NH_4Cl = CaCl_2 + \overset{\uparrow}{(NH_4)_2CO_3}$.

41. Affinity is influenced by heat. This influence may be indirect, as when, in liquefying bodies, the heat is applied to overcome cohesion; but there are many cases in which it acts directly.

Exp. 47.—Endeavor to light the gas from an ordinary burner by a hot iron rod. The gas will not ignite until the iron is at a bright red heat.

The temperature at which bodies enter into combination with the oxygen of the air, so as to produce ignition, varies greatly. No heat is sufficient to ignite iodine, chlorine, or bromine in the air or in oxygen gas. Most of the elements require to be heated before they take fire. Sulphur ignites at about 285° C.; carbonic disulphide vapor is ignited by a warm glass rod; phosphorus is ignited at about 60° C. A match tipped with phosphorus is sufficiently heated by gentle friction to ignite.

Exp. 48.—Place a slip of dried phosphorus on a chip of wood. Fill a test tube with boiling water. Touch the phosphorus with the end of the tube and it will ignite.

A certain temperature is therefore sometimes necessary to induce combination. When the chemical action is once well begun, the heat developed by the union of the bodies is usually sufficient to continue it; but, if this is not the case, or if the heat evolved be too rapidly conducted away, the action ceases.

Exp. 49.—Conduct a stream of dry ammonia gas* into the jet of a Bunsen's burner; it will burn with a pale flame, which is extinguished as soon as the burner is taken away.

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* This may be obtained by heating ordinary ammonium hydrate in a small flask, and conducting the vapor through a tube filled with small lumps of quicklime to dry it.

If the ammonia is heated by passing it through a hot tube, the flame will be continuous.

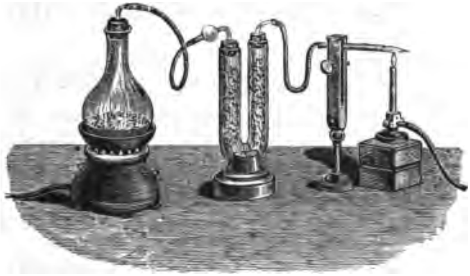

FIG. 10.

Exp. 50.—Bring a cold white plate over an ignited gas jet. Soot will be deposited, because the plate reduces the temperature below that required for the ignition of the carbon present in the flame.

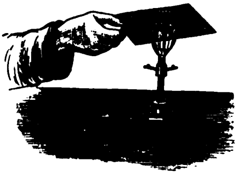

FIG. 11.

Exp. 51.—Bring a sheet of fine wire gauze over an ignited jet of coal gas. The flame is arrested at the under surface of the gauze, because the metal conducts away so much of the heat that the temperature of the gas which passes through the gauze is lower than that necessary to effect combination between the gas and the oxygen of the air. Unignited gas passes through, as may be shown by igniting it above the gauze.

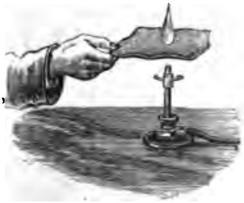

FIG. 12.

Exp. 52.—The gas may be ignited above the gauze without igniting the jet below, as shown in Fig. 12.

42. Heat also effects decomposition. We have already seen, by Exp. 25, that a mercuric oxide is decomposed by heat, although a less heat is sufficient to produce combination of the same elements. So, also, limestone, or calcium carbonate, is decomposed by strong heat into quicklime and carbonic anhydride, although the affinity between the two is at ordinary temperatures so great that quicklime exposed to the air absorbs the carbonic anhydride contained in it, and again forms calcium carbonate.

Exp. 53.—If a stream of carbonic anhydride is passed over sodium gently heated, it is decomposed with the formation of sodium oxide and carbon. On the other hand, a mixture of carbon and sodium oxide, strongly heated, yields again sodium and an oxide of carbon. At ordinary temperatures the affinities of carbon are feeble, but at white heat they are among the strongest known.

43. Chemical combination is usually attended by the evolution of heat, and sometimes also of light. When a substance combines with the oxygen of the air so rapidly as to evolve light, we call the process *combustion*, and say that the substance *burns*. Thus, we say a piece of ignited sulphur *burns;* but when a metal combines slowly with the oxygen and no light is evolved, we say the metal *corrodes*, or *rusts.* Thus, a piece of iron rusts in moist air. In chemical language, both of these processes are examples of combustion; and so, also, true combustion can take place when no oxygen is present.

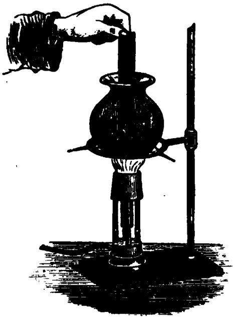

FIG. 13.

Exp. 54.—Strongly heat in a wide-mouthed flask a little sulphur, until the flask is filled with sulphur vapor. Also heat a strip of thin copper foil and plunge it quickly into the sulphur vapor. The two elements combine and evolve heat and light.

It was formerly the custom to classify bodies as *combustible* bodies and *supporters of combustion;* but these terms are manifestly inappropriate; because, when sulphur burns in air, we should have to call sulphur the combustible body, and, when copper burns in sulphur, the sulphur is the supporter of combustion. Combustion is, in fact, due to chemical combination in which both bodies play an equal or reciprocal part.

Ordinarily, coal gas may be said to burn in air, but air will also burn in an atmosphere of coal gas.

Exp. 55.—Fit a perforated cork to an ordinary lamp chimney, and attach this to a gas burner, as shown in Fig. 14. Fill a gas bag or a large bladder with air, and attach to its mouth a tube drawn out so as to yield a very small jet. Turn on the gas, and after it has escaped for some time, ignite it. Now bring the jet of the bag to the top of the chimney and force out the air. It will ignite, and may then be depressed in the chimney. The air will continue to burn at the jet.

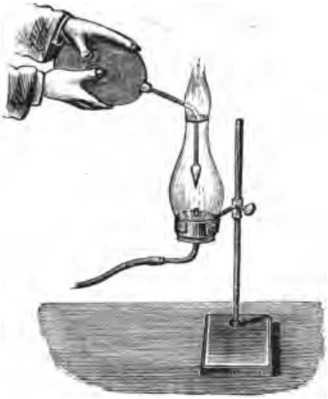

FIG. 14.

In this case, as well as in the ordinary process, the combustion takes place where the two gases meet and enter into combination.

44. The heat of combination varies with the bodies that are brought in combination and the product formed;* but it is important to observe that the same amount of heat will ultimately be evolved, whether the union takes place rapidly or slowly; only, in the latter case, it may not be possible to measure the heat.

The heat of combination may be measured in *thermal units.* A thermal unit is the heat required to raise one pound (or one gramme) of water from 0° C. to 1° C.

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* It is probable that the relation between heat and chemical action will soon become an important factor in theoretical chemistry; but, as yet, the results reached are of interest mainly to advanced students.

The following table gives some of the results obtained by burning the substances named in oxygen, chlorine, and iodine vapor.

HEAT DEVELOPED BY COMBINATION

I. WITH OXYGEN.

ONE POUND OF	COMPOUND FORMED.	THERMAL UNITS.	ONE POUND OF	COMPOUND FORMED.	THERMAL UNITS.
Hydrogen	H_2O	34462	Sulphur	SO_2	2220
Carbon	CO_2	8080	Zinc	ZnO	1330
Phosphorus	P_2O_5	5747	Iron	Fe_3O_4	1582

II. WITH CHLORINE.

Hydrogen	HCl	23783	Zinc	$ZnCl_2$	1529
Phosphorus	P_2Cl_5?	3422?	Iron	Fe_2Cl_6	1745

III. WITH IODINE.

Zinc	ZnI_2	819	Iron	Fe_2I_6	463

The ordinary combustion of wood, coals, and oils are familiar examples of combustion. These bodies are generally compounds of carbon and hydrogen. In burning, they are first decomposed, and then unite with the oxygen of the air to form water and carbonic anhydride.

We may also remark that heat is frequently evolved in the processes of substitution and double decomposition; and sometimes also by direct decomposition, as when gun cotton explodes.*

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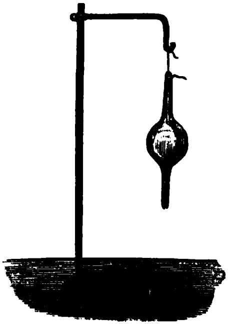
* In considering these relations of heat, we may have regard to three points: (1) The temperature of ignition; (2) The heat of combination, or the calorific value of a substance; and (3) The temperature attained. This last may be found theoretically, by dividing its available calorific value by the product found by multiplying together the weight of the compound formed and its specific heat. Thus, one pound of hydrogen burning in oxygen evolves 34462 thermal units. The 9 pounds of steam which are formed render latent 537 × 9 = 4833 thermal units. The calorific value of the hydrogen remaining will be 34462 — 4833 = 29629 thermal units, which are available for raising the temperature of 9 pounds of steam. Now, as the specific heat of steam is 0.48, it will require 0.48 × 9 = 4.32 thermal units to raise the 9 pounds 1° C. Finally, dividing the available calorific value 29629 by 4.32, we obtain 6930° C., as the temperature to be attained by hydrogen burning in oxygen. It is needless

45. Affinity is sometimes influenced by light. Light plays an important part in the chemical processes of nature, being necessary to the vigorous growth of plants, and contributing not a little to the health of animals. It is not without influence in the operations of a chemical laboratory.

Exp. 56.—Fill a clear glass bottle with a mixture of equal parts of chlorine and hydrogen, in a darkened room, and cork the bottle tightly. Wrap it in thick folds of cloth, and, having brought it out into bright sunlight, stand at a distance and pull off the cloth by means of a string previously attached to it. The gases will instantly combine with explosive violence, and shatter the bottle into a thousand fragments.

This experiment succeeds best when the mixture is obtained by the electrolysis of hydrochloric acid. Collect the mixed gases in small bulbs of thin glass, which are easily made from glass tubing. (Fig. 15).



FIG, 15.

In diffused light the action is prolonged, and the union takes place without explosion. In darkness, they do not combine at all.

Exp. 57.—Add a solution of silver nitrate to hydrochloric acid. (Fig. 16.) A white precipitate of silver chloride will be formed. This silver chloride, exposed for a short time to the sunlight, becomes violet, then black. The silver chloride loses part of its chlorine.

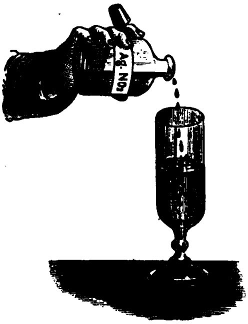


FIG. 16.

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to say that this is never reached, as a large portion of the heat is dissipated. When hydrogen burns in air, the nitrogen has to be warmed, and the temperature attained is about 2740° C. Here also, if the blast of air is too strong, a less temperature will be reached; and it is easily conceivable that a body, by very slow combustion (rotting), may expend nearly all its available heat on surrounding objects.

Light, therefore, acts also as a decomposing agent. The property which light has of darkening silver chloride and silver iodide has been applied in photography.

Exp. 58.—Dip unsized paper in brine made of common salt, and then dry it. By means of a light brush, cover one side of this with a solution of silver nitrate, and dry it in a darkened room. The surface of the paper will be covered with a film of silver chloride. Now oil an ordinary engraving so as to render it translucent. Lay this *closely above* the silvered side of the paper, and expose it to bright sunlight for ten minutes. A reversed, or negative, copy of the picture will be found on the paper. It may be rendered permanent by soaking it for a while in a solution of sodium hyposulphite, to dissolve the silver chloride which has not been changed by the light, and then by washing the paper in water, to remove the hyposulphite. (See **Exp. 125**).

On the other hand, light is frequently evolved by chemical combination. This is, in fact, the source of most of our artificial lights.

46. Affinity is influenced by electricity. Frictional electricity will effect the combination of some elements. We may use for this purpose a strong glass tube, called an eudiometer (Fig. 17), open at one end and closed at the other. Through the closed end are melted two platinum wires, whose points are separated so that a spark from a Leyden jar may pass between them.

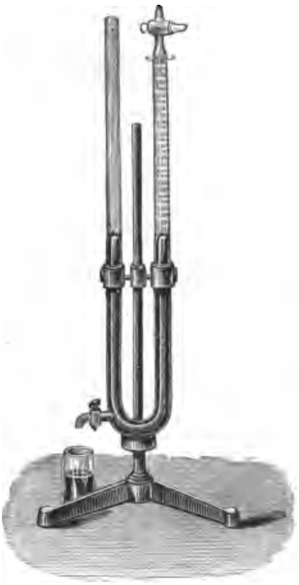

FIG. 17.

Exp. 59.—Fill the eudiometer with mercury: then pass into it a measured volume of oxygen and two equal measures of hydrogen, taking care that the mixture does not more than half fill the tube. Close the open end of the tube by a caoutchouc stopper. Now pass an electric spark between the platinum points. A flame will pass down through the gas, showing that combination has taken place. On removing the caoutchouc stopper, the mercury will rise and fill the tube.

If this experiment be modified by inclosing the closed arm of the eudiometer in a larger tube which is kept filled with the vapor of amylic alcohol (a liquid which boils at 132° C.), the water will not condense, but remain as steam. It will then be found, on removing the stopper, that the steam formed by the union of the two gases fills two-thirds of the volume previously occupied by the three volumes of mixed oxygen and hydrogen.

Therefore, when two volumes of hydrogen combine with one volume of oxygen, they condense to two volumes of aqueous vapor.

47. The galvanic current is an energetic agent in producing decomposition of compounds. This mode of decomposition is called *electrolysis*.

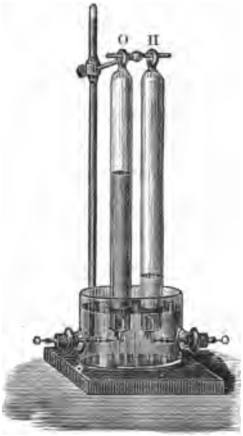

Fig. 18.

Fig. 18 represents an apparatus which may be used to show the decomposition of water. It consists of a glass vessel having two corked openings, through which are passed two wires terminating in platinum electrodes. The vessel being filled with water slightly acidulated with sulphuric acid, two glass tubes, also filled with water, are inverted over the electrodes, and the outer wires are connected with some constant battery. Four Grove's cells are sufficient to cause a rapid decomposition of the water.

Hydrogen rises from the negative electrode, and oxygen from the positive. As water absorbs more oxygen than hydrogen, the gases evolved can not be accurately measured until the water is saturated with the gases. It will then be found that exactly twice as great a volume of hydrogen is evolved as of oxygen. This result confirms Exp. 59.

Other liquids may be decomposed by the same apparatus. Hydrochloric acid evolves hydrogen at the negative and chlorine at the positive electrode. After the liquid is saturated with the gases,—which will require some time if the quantity is considerable,—the two gases are evolved in equal volumes; that is, hydrochloric acid contains one volume of hydrogen and one of chlorine. If both gases are collected in an eudiometer and exploded, it will also be found that they again unite, without condensation, to two volumes.

Fused metallic chlorides yield the metal at the negative and the chlorine at the positive electrode.

If, however, an aqueous solution be used, it may act on one or both of the constituents evolved, and cause a *secondary* action. An aqueous solution of iodide of potassium is easily decomposed; but, as soon as the potassium is liberated, it decomposes the water, forming potassium oxide, and hydrogen gas is liberated at the negative electrode.

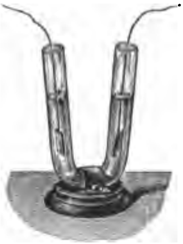

FIG. 19.

Exp. 60.—Fill a U tube with a solution of sodium sulphate, colored by an infusion of red cabbage, and plunge the platinum electrodes in each arm. The fluid at the negative electrode will be colored green, and at the positive electrode, red. We have already learned that these changes in color indicate the presence of an alkali and an acid.

The action is somewhat complex. To explain it we may suppose the sodium sulphate to have the formula, Na_2SO_4. The galvanic action breaks this up into sodium, Na_2, and into SO_4. This last body has never been obtained in a free state, but it is convenient to suppose its existence here. The sodium collects at the negative pole, and the SO_4 at the positive. At both poles a secondary action takes place. A molecule of water is decomposed; its hydrogen unites with the SO_4 to form H_2SO_4, or sulphuric acid; its oxygen, with the sodium to form sodium oxide, Na_2O. This unites with another molecule of water, forming sodium hydrate, Na_2O, H_2O, or $2NaHO$.

48. Since unlike electricities attract each other, the bodies which collect at the negative electrode are called positive, and those which collect at the positive electrode are called negative. These terms are merely relative, as chlorine is electro-positive with reference to oxygen or sulphur, and electro-negative with reference to hydrogen and the metals. The metals and their oxides are generally electro-positive; the non-metals, the semimetals, and the acid radicals, generally electro-negative.

Exp. 61.—Place in a series of test tubes solutions of the nitrates of (1) lead, (2) copper, (3) mercury, (4) silver. A globule of mercury placed in (4) will reduce the silver, and a nitrate of mercury will be formed. Similarly, a slip of bright copper in (3), of iron in (2), or of zinc in (1), will reduce metallic mercury, copper, or lead, and form the corresponding nitrates, thus exhibiting a difference of affinity which may be referred to the difference in electrical relations. Zinc will reduce most metals from their acid solutions. Sodium amalgam is a still more powerful reducing agent for the metals.

In many such cases of reduction, the water of the solution is first decomposed, its oxygen uniting with the zinc or the sodium, and its *nascent hydrogen* with the acid radical previously combined in the metallic salt. Such reactions are secondary, like those described in Exp. 60.

Generally speaking, the affinities between elements of widely different electricities, as between the metals and oxygen or chlorine, are the strongest; but many stable compounds are known in which both the elements are reckoned as negative; as, SO_2, I_2O_5.

The following is a portion of Berzelius's electro-chemical series, in which any element, counting from oxygen, is electro-negative to those that follow it, and electro-positive with reference to those that precede it.

—	+
Oxygen	Caesium
Sulphur	Potassium
Nitrogen	Sodium
Fluorine	Zinc
Chlorine	Iron
Bromine	Copper
Iodine	Silver
Phosphorus	Mercury
Carbon	Platinum
Antimony	Gold

Hydrogen
±

The galvanic current is maintained by a chemical action which takes place within the cell, proceeding from the plate which is most easily acted upon by the fluid portion of the battery. Not only this, but the quantity of electricity developed is so related to the energy and amount of the chemical action, that the proportions between them can be expressed numerically.

49. There is, therefore, an intimate relation between the force of affinity and the forces of heat, light, and electricity. Affinity may produce heat, light, or electricity. It may be set in action by either of them, and cause bodies to unite, or be so weakened that its compounds are decomposed. Heat may also generate electricity, and electricity be made to evolve heat and light. For these reasons these forces are called the *correlative forces.*

Finally, there are so many cases in which the disappearance of one of these forces is marked by the evolution of another in numerical proportions, that we are justified in the conclusion that these forces are convertible the one into the other; that affinity, for instance, may reappear as heat, light, or electricity, singly or simultaneously. If this be true, we are not to suppose that when we can no longer trace the action of a force, it has been annihilated, but that it has changed to some other form of force. Force is, therefore, indestructible.

The correlative forces are all thought to be modes of motion impressed upon the ultimate particles of matter in bodies. The difference in the mode of motion determines whether heat, light, electricity, or affinity is produced. Affinity seems to stand in closer relation to electricity than to either of the other forces.

Recapitulation.

The characteristics of chemical affinity:

It varies with the kind of matter;
with the relative mass of matter;
is strongest in the nascent state of matter;

It varies with the state of cohesion;
with the solubility of the product;
with the volatility of the product.

A fluid state necessary to effect combination.

It is influenced by adhesion;
by the state of division of matter.

Surface action induces combination.

It is influenced by heat,
so as to effect combination;
so as to effect decomposition.

It is influenced by light,
so as to effect combination;
so as to effect decomposition.

It is influenced by electricity,
so as to effect combination;
so as to effect decomposition.

Correlatively: It may produce heat, light, and electricity.

CHAPTER III.*

CHEMICAL PHILOSOPHY AND NOMENCLATURE.

50. The facts of chemistry are established by experiment, and are capable of being reproduced. They find a practical application in the arts, which is altogether independent of any explanation that may be made of them. When, however, we attempt to reason upon these facts, to classify them, to interpret them, we at once begin to form theories. A theory which renders a reasonable explanation of a great number of facts is useful (1) because it enables us to group them into a system, and (2) because it often leads to new experiments and to the discovery of other facts.

We are liable to three errors: (1) we may assume that to be a fact which has no existence; or (2) we may sometimes mistake a phenomenon, so as to imagine that to be a cause which is only an effect of some unknown cause; or, finally, (3) we may become so accustomed to the language of theory as to mistake its definitions for facts. Once assured of our facts, we may be certain that they are immutable. Nevertheless, it has often happened that statements which have been accepted as facts have been rejected because they have been found to be false; and that one theory has been displaced by another which interprets a greater number of facts.

51. We know nothing of the manner in which the ultimate particles of matter are arranged together: we *believe* that they are arranged in accordance with certain theories which we shall now proceed to develop.

All masses of matter may be subdivided into very small particles; but it is probable that there is a limit to this subdivision, and that all bodies are made up of particles so infinitesimally small that they are inappreciable to our senses. By the terms of this theory,

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* To TEACHERS.—The author advises that young students in chemistry should study, on the advance, only so much of this chapter as is necessary to accept the *fact* of atomicity, and the notation and nomenclature of compounds. The full discussion of chemical philosophy may be deferred until the class has reached Chapter XI. Mature students will find it best to master the subject at this point, where it logically belongs. It is not exceptionally difficult.

A molecule is the smallest particle of matter capable of existing in the free state:

An atom is the smallest particle of matter that is capable of entering into or existing in a state of chemical combination.

If we subdivide hydrochloric acid, the least particle that we can obtain, without destroying the identity of the acid, is a *molecule;* but we know that this molecule contains still smaller particles of hydrogen and chlorine. Compound bodies contain the atoms of different elements, united to form *compound molecules;* as, HCl. We suppose, also, that the atoms of the same element may unite to form *elementary* molecules; as, H_2 or Cl_2.

52. It is also believed (1) that the atoms of the same element are exactly alike, and that they have a definite size, shape, and weight; (2) that the atoms of different elements are always unlike, differing in weight and, perhaps, in form; and (3) that equal volumes of all aëriform bodies contain, at the same temperature and pressure, an equal number of molecules.* (4) It also naturally follows that one molecule of any aëriform body must occupy a certain definite space, which is called its *molecular volume,* and that *all molecular volumes are equal.*

Hereafter it will be assumed that all gases are measured when at the temperature of the freezing point of water, and under the pressure of one atmosphere. These are called the *normal* conditions of temperature and pressure.

The following table gives the weight in grammes of 11.2 litres of the following elements, when in the aëriform state, at the normal temperature and pressure:

Hydrogen,	1.	Oxygen,	16.	Phosphorus,	62.
Chlorine,	35.5	Sulphur,	32.	Arsenic,	150.
Bromine,	80.	Selenium,	79.5	Mercury,	100.
Iodine,	127.	Nitrogen,	14.	Cadmium,	56.

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* This is known as Avogadro's Law.

These numbers are also the *relative weights* of equal volumes, whether those volumes are measurable or infinitesimal. The student must always remember that a molecular volume or an atomic weight is a definite quantity, although very small.

53. **The absolute weight or volume** of any atom is not certainly known.* The combining numbers given on pp. 12 and 13 express the *relative weights* of the atoms, and are called the *atomic weights.* These numbers have been obtained by several extended series of observations. The principal considerations that have led to their adoption are the following:

Hydrogen is the lightest element known. We may therefore take it as the unit by which other substances may be compared; that is, as the standard unit (1) for the specific gravity of gases; (2) for atomic weight; (3) for molecular volume; and, as we shall see hereafter, (4) for the unit of combining power.

We have learned (p. 46) that two volumes of hydrochloric acid gas contain one volume of hydrogen and one of chlorine. Since all molecular volumes are equal, two molecular volumes of hydrochloric acid gas must contain one molecular volume of hydrogen and one of chlorine. On analysis, we find that one molecular volume of hydrochloric acid gas yields one atom of chlorine and one atom of hydrogen. The two molecular volumes of the acid gas, therefore, contain two atoms of hydrogen and two of chlorine. A molecule of hydrogen must, therefore, contain two atoms, and a molecule of chlorine two atoms. Therefore, if the atomic weight of hydrogen be assumed as unity, its molecular weight will be 2, and its molecular volume also 2.

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*Physicists have carried the doctrine of molecules further. They find that most of the phenomena exhibited by gases, such as their elastic force, can be satisfactorily explained on the assumption that these bodies consist of perfectly elastic particles, which are perpetually colliding against each other, and against the sides of the vessel which contains them. They have even gone so far as to make an attempt to measure the size and mass of the molecules, the distances between them, and the rate of their motion. The following are Maxwell's results. Two hundred million hydrogen molecules in a row would measure little more than one centimetre. In a cubic centimetre of any gas under the normal conditions of temperature and pressure, there are 19,000,000,000,000,000,000 molecules. The velocity of the hydrogen molecule is 1,843 metres per second. The mass of a molecule of hydrogen is 46 ten-million, million, million millionths of a gramme. The masses of the molecules of all gases are as their atomic weights; hence, the velocity of gases will be inversely proportional to the square roots of their atomic weights. The spaces which separate the molecules are much larger than the molecules themselves. Reckoned in hundred billionths of a metre, a molecule of hydrogen would have a diameter of 58, while the mean path which it describes is 9,650, and the number of collisions it encounters per second amount to 17,750 millions.

54. Since all molecular volumes are equal, the molecular volume of any aëriform substance must be 2. The density of aëriform bodies is the relative weight of one volume; hence, the molecular weight of any aëriform body must be double its density. The molecular weights of the elements previously named are:

Hydrogen,	2.	Nitrogen,	28.	Phosphorus,	124.
Chlorine,	71.	Oxygen,	32.	Arsenic,	300.
Bromine,	160.	Sulphur,	64.	Mercury,	200.
Iodine,	254.	Selenium,	159.	Cadmium,	112.

If all the elementary molecules had the same number of atoms as the hydrogen molecule, the atomic weights of the elements would be identical with their densities. This is the case with most of the elements that can be obtained in the aëriform state. *In all cases* the molecular weight of an element is equal to the product of its atomic weight by the number of atoms in one elementary molecule. Hence, if we know any two of these quantities, we can find the other by a simple calculation.

55. The atomic weight of any element is obtained by comparing the results of the analysis of many compounds of that element. When the compound is a gas, the density is obtained by direct experiment, and the relative proportions of its constituents are easily determined.

Two volumes of each of the following compounds of hydrogen are found to yield these results:

WEIGHTS OF TWO VOLUMES	DENSITY	NAME OF COMPOUND	PROPORTIONS BY WEIGHT	PROPORTIONS BY VOLUME	FORMULÆ
36.5	18.25	Hydrochloric acid.	H, 1 + Cl, 35.5	H, 1 + Cl, 1	HCl
18.	9.	Perfect steam.	H, 1 + O, 8.	H, 2 + O, 1	H_2O
17.	8.5	Ammonia.	H, 1 + N, 4.7	H, 3 + N, 1	H_3N
16.	8.	Marsh gas.	H, 1 + C, 3.	H, 4 + C, 1	H_4C

If we consider only the weights which unite with one part of hydrogen, the atomic weight of chlorine is 35.5; of oxygen, 8; of nitrogen, 4.7; and of carbon, 3.

The molecular weight of each of these compounds is equal to the weight of two volumes. The molecular weight is also equal to the sum of the atomic weights of its constituents. If these two do not agree, the atomic weights assigned are incorrect.

The molecular weight of hydrochloric acid is 36.5: this is also the sum (35.5 + 1) of the combining weights of chlorine and hydrogen. Therefore, 35.5 is the atomic weight of chlorine.

The molecular weight of steam is 18; but the sum (1 + 8) of the combining weights is half of this; hence, one molecule of steam must contain 2 parts of hydrogen and 16 of oxygen.

So, also, 17 parts, by weight, of ammonia must contain 3 parts of hydrogen and 14 of nitrogen; and 16 parts, by weight, of marsh gas must contain 4 parts of hydrogen and 12 of carbon.

As we know of no hydrogen compounds in which chlorine, oxygen, nitrogen, and carbon unite in less proportion than 35.5, 16, 14, and 12, these numbers are adopted as the atomic weights of these elements.

56. The atomic weights of those elements that do not form compounds with hydrogen are fixed by a comparison of their compounds with chlorine or some other element.

We are aided in this comparison (1) by the fact that many similar compounds are *isomorphous;* that is, they form crystals which have precisely the same form. Thus, many of the compounds of magnesia, zinc, and cadmium are isomorphous. If we can determine the number of atoms in one molecule of either of these bodies, it is fair to suppose that the others contain an equal number and have a similar molecular structure.

(2) A more general aid in determining the atomic weight of an element is by means of its specific heat. The specific heat of a body is the fraction which expresses the amount of heat required to raise a unit weight of the substance as compared with that required to raise an equal weight of water from 0° C. to 1° C. It is found that the product of the atomic weights by the specific heats of the several elements gives a constant quantity, which is called the specific heat of atoms. The mean value of this product is 6.34, and any small deviation from it is thought to result from the unavoidable errors of experiment.

These relations are shown in the following table:

	SPECIFIC HEAT.		ATOMIC WEIGHT.		
Sodium,	0.29840	×	23	=	6.75
Sulphur,	0.20259	×	32	=	6.48
Arsenic,	0.08140	×	75	=	6.11
Phosphorus,	0.18870	×	31	=	5.85
Mercury,	0.03192	×	200	=	6.38
Cadmium,	0.05669	×	112	=	6.35
Zinc,	0.09555	×	65	=	6.21
Average					6.34

Carbon, boron, and silicon are exceptions to this law.

There are also exceptions to the law of vapor densities which can not be explained in the present state of the science.

(3) If we divide the molecular weights of the elements by the atomic weights, we shall find the number of atoms in each molecule in the aëriform state.

Mercury, zinc, and cadmium have each one atom in a molecule. Their vapor densities are half their atomic weights, and their atomic volumes double those of hydrogen.

Phosphorus and arsenic have each four atoms in a molecule. Their vapor densities are double their atomic weights, and their atomic volumes are only half those of hydrogen.

Most of the other elements are supposed to contain two atoms in each molecule. Their vapor densities are equal to their atomic weights, and their molecular volume is equal to that of hydrogen = 2. This last statement must be regarded as hypothetical in regard to those elements which can not be completely vaporized, as carbon, silicon, etc.

57. If these considerations are accepted, we must represent hydrochloric acid by the formula, HCl; water, by H_2O; ammonia, by H_3N; and marsh gas, by H_4C. Each separate symbol represents (1) one atomic volume, (2) one atomic weight, and (3) the specific gravity of each element in the aëriform state referred to hydrogen as unity. (4) The numbers below each letter show how many times the atom is taken to form the compound molecule.

Each formula represents (1) one compound molecule: its molecular weight is the sum of the atomic weights of its constituents. (2) It also represents two volumes, and therefore its specific gravity, in the aëriform state, is half the molecular weight.

58. These formulæ are called *typical formulæ*, because they may be severally taken as types or examples of a large number of compounds having a similar molecular structure. Thus, we may have:

Hydrochloric Acid HCl	Water H_2O	Ammonia H_3N	Marsh Gas H_4C
Hydrobromic Acid HBr	Hydrogen Sulphide H_2S	Hydrogen Phosphide H_3P	Hydrogen Silicide H_4Si
Hydriodic Acid HI	Hydrogen Selenide H_2Se	Hydrogen Arsenide H_3As	

59. We can not fail to notice that these groups are distinguished by the number of atoms of hydrogen which combine with one atom of the other element. Chlorine has a combining power sufficient to fix one atom of hydrogen; oxygen has a combining power sufficient to fix two atoms of hydrogen; nitrogen has a combining power of 3; carbon, of 4. Atoms which have an equal combining power are said to be equivalent, or to have the same atomicity; that is, they may replace each other, atom for atom.

Thus, if we decompose hydriodic acid by chlorine, we may represent the reaction, $HI + Cl = HCl + I$. Chlorine and hydrogen have each the same combining power. The metals — potassium, sodium, and silver — form compounds which contain one atom of chlorine. They displace one atom of hydrogen in hydrochloric acid, and are equivalent to it: $HCl + Na = NaCl + H$.

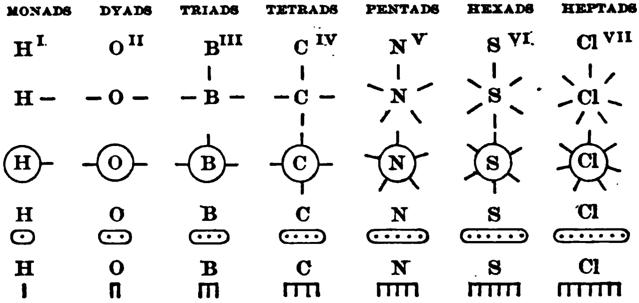
On the other hand, if we decompose water by chlorine, the reaction is, $H_2O + Cl_2 = 2HCl + O$. Two atoms of chlorine are required to displace one atom of oxygen; hence, the oxygen atom has twice the combining power of chlorine, or can fix two atoms of hydrogen. So, also, one atom of sulphur, calcium, or zinc combines with two atoms of chlorine or with one of oxygen, and has double the combining power of hydrogen, or an atomicity of 2.

60. All the elements may be arranged in seven groups, according as they combine with 1, 3, 5, 7 atoms or 2, 4, 6 atoms of hydrogen or of chlorine. The elements which make up these groups are called:

Monads or univalent, whose atomicity = 1 as H'
Dyads or bivalent, " " = 2 as O''
Triads or trivalent, " " = 3 as B'''
Tetrads or quadrivalent, " " = 4 as C^{IV}
Pentads or quinquivalent, " " = 5 as N^{V}
Hexads or sexivalent, " " = 6 as S^{VI}
Heptads or septivalent, " " = 7 as Cl^{VII}

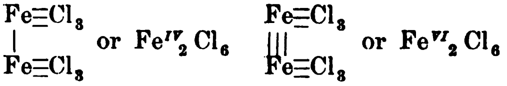
61. The equivalence or atomicity of an atom is represented by accent marks or Roman numerals placed above the symbol. These marks do not multiply the atoms, and should not be confounded with the figures placed below the symbols.

The atomicity is sometimes expressed graphically by lines called *bonds* radiating from a symbol, or from some figure which represents an atom. The following are examples:



62. The atomicities of all of the elements have not been experimentally determined, and are open to revision. There are also apparent variations in the equivalency of many elements, which are difficult of explanation. Thus, nitrogen is trivalent in ammonia, NH_3, and quinquivalent in ammonium chloride, NH_4Cl. Chlorine is usually regarded as a monad element, but it appears also to act as a heptad. So, also, iron is variously classed a bivalent, quadrivalent, and sexivalent element.

Generally, but not always, the atomicity assigned to an element is that derived from its highest compound with monad elements, and any lower compound is said to be *unsaturated*, or that the element has one or more of its bonds unsatisfied. Such unsaturated compounds are frequently unstable, and tend to form the higher, saturated compound. Thus, in ferrous chloride, $Fe^{II}Cl_2$, the iron is apparently bivalent, but on exposure to the air it forms ferric compounds which are either quadrivalent or sexivalent.



$$\begin{array}{l} Fe\equiv Cl_3 \\ | \\ Fe\equiv Cl_3 \end{array} \text{ or } Fe^{IV}_2Cl_6 \qquad \begin{array}{l} Fe\equiv Cl_3 \\ ||| \\ Fe\equiv Cl_3 \end{array} \text{ or } Fe^{VI}_2Cl_6$$

We find, however, that the same element almost always exhibits a valency which may be represented either by an odd or by an even number. Those elements whose valency can be represented by 1, 3, 5, or 7, are called *perissads;* those whose valency is 2, 4, 6, or 8, are called *artiads.* It is also noticeable that the sum of the bonds, in a stable, saturated molecule, is always an *even* number.

Although there are many apparent contradictions and unexplained anomalies in the doctrine of atomicity, it bids fair to be of immense importance in theoretical chemistry.

The following table gives the atomicities usually assigned, and also groups the elements in accordance with their more striking properties.

TABLE OF THE ELEMENTS.

PERISSADS.

Monads.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Hydrogen	H	1.
Fluorine	F	19.
Chlorine	Cl	35.5
Bromine	Br	80.
Iodine	I	127.
Lithium	Li	7.
Sodium	Na	23.
Potassium	K	39.1
Rubidium	Rb	85.4
Caesium	Cs	133.
Silver	Ag	108.

Triads.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Boron	B	11.
Indium	In	113.4
Gold	Au	197.
Thallium	Tl	204.

Pentads.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Nitrogen	N	14.
Phosphorus	P	31.
Vanadium	V	51.2
Arsenic	As	75.
Antimony	Sb	122.
Bismuth	Bi	210.
Niobium	Cb	94.
Tantalum	Ta	182.

ARTIADS.

DYADS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Oxygen	O	16.
Calcium	Ca	40.
Strontium	Sr	87.6
Barium	Ba	137.
Magnesium	Mg	24.
Zinc	Zn	65.2
Cadmium	Cd	112.
Copper	Cu	63.4
Mercury	Hg	200.
Glucinum	G	9.4
Thorinum	Th	57.9
Yttrium	Y	61.6
Lanthanum	La	93.6
Didymium	D	95.
Erbium	E	112.6

TETRADS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Carbon	C	12.
Silicon	Si	28.
Titanium	Ti	50.
Tin	Sn	118.
Aluminium	Al	27.4
Gallium	Ga.	69.9
Zirconium	Zr	89.6
Cobalt	Co	58.8
Nickel	Ni	58.8
Cerium	Ce	92.
Uranium	U	120.
Lead	Pb	207.
Palladium	Pd	106.
Platinum	Pt	197.4
Rhodium	Rh	104.4
Iridium	Ir	198.

HEXADS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Ruthenium	Ru	104.4
Osmium	Os	199.2
Molybdenum	Mo	96.
Tungsten	W	184.
Sulphur	S	32.
Selenium	Se	79.4
Tellurium	Te	128.
Chromium	Cr	52.2
Manganese	Mn	55.
Iron	Fe	56.

NOTE.—This list is taken from "Watt's Dictionary of Chemistry." The atomic weights do not always accord with those given on pp. 12 and 13.

63. We may suppose that the elementary molecules consist of two atoms whose bonds mutually satisfy each other, graphically represented thus:

H--H, Hydrogen. O==O, Oxygen. N≡≡N, Nitrogen.

In compounds, any atom may have its bonds satisfied by another atom having an equal atomicity; or by several atoms, the sum of whose bonds is equal to that of the first; thus, a dyad may be saturated by two monad atoms or by one dyad atom; a triad by a triad, by three monads, or by one monad plus one dyad, etc. Thus, we may represent graphically:

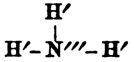
Mercuric oxide, $Hg''=O''$

Water, $H'-O''-H'$

Sodium hydrate, $Na'-O''-H'$

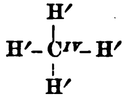
Carbonic anhydride, $O''=C^{IV}=O''$

Ammonia,



$$\begin{array}{c} H' \\ | \\ H'-N'''-H' \end{array}$$

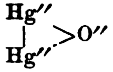
Marsh gas,



$$\begin{array}{c} H' \\ | \\ H'-C^{IV}-H' \\ | \\ H' \end{array}$$

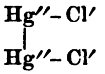
64. In compounds, a portion of the bonds of a multivalent atom may be satisfied by another atom of the same element. Examples of this may be represented graphically, thus:

Mercurous oxide,



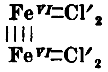
$$\begin{array}{l} Hg'' \\ | \quad >O'' \\ Hg'' \end{array}$$

Mercurous chloride,



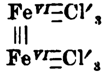
$$\begin{array}{l} Hg''-Cl' \\ | \\ Hg''-Cl' \end{array}$$

Ferrous chloride,



$$\begin{array}{l} Fe^{VI}=Cl'_2 \\ |||| \\ Fe^{VI}=Cl'_2 \end{array}$$

Ferric chloride,



$$\begin{array}{l} Fe^{VI}\equiv Cl'_3 \\ ||| \\ Fe^{VI}\equiv Cl'_3 \end{array}$$

65. The theory of atomicities has received an important extension in the doctrine of *radicals.*

Suppose an atom of hydrogen were removed from the saturated molecules, HCl, H_2O, H_3N, H_4C: there would remain, Cl, HO, H_2N, H_3C. These residues are evidently unsaturated, and are able to combine with an atom of hydrogen to reproduce the original compound, or with any other monad to form such compounds as, Cl_2, KCl, KHO, KH_2N, H_3ClC. Such unsaturated residues, or groups of atoms, are called *radicals.*

Compound radicals act precisely like the elements: they do not generally exist in a free state in nature, but sometimes may combine with a similar group to form saturated molecules. If but one hydrogen atom is removed, the radical is univalent; if two, bivalent; if three, trivalent; and so, generally, the equivalence of the radical is the number of unsatisfied bonds.

From marsh gas we may derive four radicals, and obtain by their union with elementary atoms, or with other radicals, a great number of compounds. Thus, we may have from H_4C, = marsh gas, a saturated compound.

RADICALS.	NAME.	FORMING COMPOUNDS WITH	
		CHLORINE.	OTHER RADICALS.
$(CH_3)'$ univalent	Methyl	CH_3Cl, methyl chloride	$(CH_3)_2$, free methyl.
$(CH_2)''$ bivalent	Methylene	CH_2Cl_2, methylene chloride.	$(CH_2)_2O_2$, dioxymethylene.
$(CH)'''$ trivalent	Formyl	$CHCl_3$, chloroform.	CHO, O, C_2H_5, formic ether.
$(C)^{IV}$ quadrivalent	Carbon	CCl_4, tetra-chloride of carbon.	CH_4, marsh gas.

66. The term radical is further applied to any group of atoms which is common to a series of allied compounds. We may thus have an almost infinite series of radicals, which are for the most part purely hypothetical, and which we do not expect to obtain in an isolated form. Among those recognized in inorganic chemistry, that have received names, are the following:

$(HO)'$	hydroxyl.	$(NO_2)'$	nitryl.
$(HS)'$	hydrosulphuryl.	$(NO)'$	nitrosyl.
$(H_4N)'$	ammonium.	$(SO_2)''$	sulphuryl.
$(H_2N)'$	amidogen.	$(CO)''$	carbonyl.
$(CN)'$	cyanogen.	$(PO)'''$	phosphoryl.

The names of all compound radicals, except the three given above, end in *yl*. The radicals recognized in organic chemistry are so numerous that this branch of the science has been called the chemistry of compound radicals.

67. The nomenclature and notation of compounds are at present in a confused state. This arises from the fact that two principal systems are in common use: the older, devised by Lavoisier and Berzelius, is based mainly on the structure of the oxygen compounds, and regards all ternary oxides as made up of two groups of binary oxides; as, $BaO + SO_3 = BaO, SO_3$. This is called the *dualistic* system.

The newer system regards every molecule as a unit; as, $BaSO_4$, and is called the *unitary* or *molecular* system.

68. Formulæ are called *empirical* when they simply express the results of analysis in atomic symbols, without endeavoring to denote the manner in which the atoms are united; and *rational*, if they endeavor to represent the manner in which the atoms are grouped together in a compound. There can be but one empirical formula of a substance, but there may be as many rational formulæ of any compound as there are different views respecting its molecular structure. The principal of these rational formulæ are: (1) the *dualistic*, representing the theory of Berzelius; (2) the *typical*, in which the grouping is referred to representative compounds called types; such as, H_2, HCl, H_2O, H_3N, H_4C; and (3) the *structural*, which are an extension of the typical by including the compound radicals. All of these formulæ are useful; but the student must bear in mind that no one of them represents the actual position or grouping of the atoms in a complex formula with absolute certainty.

69. According to the dualistic theory, all binary oxides may be classed in three groups: bases, indifferent bodies, and acids.

Bases are electro-positive binaries, which are formed by the union of oxygen with a metal. Acids are electro-negative binaries, which are generally formed by the union of oxygen with a non-metal. The soluble acids have a sour taste, and redden litmus paper; the soluble bases have frequently an acrid taste, and restore the color of reddened litmus paper. The strongest bases are called the alkalies: they are the oxides of the potassium group.

The two groups are further characterized by the fact that they combine together to form ternary compounds called *salts*. Thus, BaO is a base, barium oxide; SO_3 is an acid, sulphuric acid. Both these may be obtained in an isolated form. If they are heated together they form BaO, SO_3, which is a salt called barium sulphate.

An indifferent body is one that either (1) will combine with no other, or (2) that sometimes plays the part of a base and sometimes that of an acid. Water is an indifferent body: it combines with barium oxide to form barium hydrate, BaO, H_2O; it also combines with sulphuric anhydride to form hydric sulphate, H_2O, SO_3.

70. The later theories use the same terms, but with a different meaning. Oxides that do not contain hydrogen are called *anhydrides.* The metallic oxides, like K_2O, CaO, HgO, are called *basic anhydrides;* and the non-metallic oxides, like SO_3, N_2O_5, are called *acid anhydrides.* These are named like other binary compounds:

BASIC ANHYDRIDES.		ACID ANHYDRIDES.	
Na_2O	Sodium oxide.	SO_2	Sulphurous anhydride.
Ag_2O	Silver oxide.	SO_3	Sulphuric anhydride.
BaO	Barium oxide.	Cl_2O	Hypochlorous anhydride.
CaO	Calcium oxide.	Cl_2O_3	Chlorous anhydride.
FeO	Ferrous oxide.	N_2O_3	Nitrous anhydride.
Fe_2O_3	Ferric oxide.	N_2O_5	Nitric anhydride.
Hg_2O	Mercurous oxide.	I_2O_5	Iodic anhydride.
HgO	Mercuric oxide.	I_2O_7	Periodic anhydride.

71. These anhydrides may combine with water, forming *hydrates.* Formerly it was supposed that these hydrates contained the water molecule, H_2O; but now it is generally thought that they bear only a typical relation to water, containing, perhaps, its radical hydroxyl; thus, $BaO + H_2O = Ba(OH)_2$; $SO_3 + H_2O = SO_2(OH)_2$.

In accordance with this view, a basic hydrate is a compound of hydrogen and a positive atom or radical united by oxygen. These hydrates are formed on the type of one or more molecules of water.

Type, H_2O.	Type, $2H_2O$.
$\left.\begin{matrix}K'\\H'\end{matrix}\right\}O''$ Potassium hydrate.	$\left.\begin{matrix}Ca''\\H'_2\end{matrix}\right\}O''_2$ Calcium hydrate.

Or we may consider these bodies as compounded with hydroxyl; thus, $K\text{–}OH$; $Ca''(OH)'_2$, as if derived from water, $H\text{–}OH$, taken as often as is necessary.

72. All true acids are compounds of hydrogen with a negative atom or radical. In the binary acids, like HCl, HI, this union is direct. These acids all receive the termination *ic*, as HCl, hydrochloric acid. In the ternary acids the union is effected by a linking atom of oxygen.

Some acids are formed on the type of one molecule of water; as:

Nitric acid, H_2O, N_2O_5 or HNO_3 or $\begin{matrix}NO'_2\\H'\end{matrix}{>}O''$ or $(HO)'NO'_2$.

Nitrous acid, H_2O, N_2O_3 or HNO_2 or $\begin{matrix}NO'\\H'\end{matrix}{>}O''$ or $(HO)'NO'$.

Others are on the type of two molecules; as, $(H_2O)_2$:

Sulphuric acid, H_2O, SO_3 or H_2SO_4 or $\begin{matrix}SO''_2\\H'_2\end{matrix}{>}O''_2$ or $(HO)'_2SO''_2$.

Sulphurous acid, H_2O, SO_2 or H_2SO_3 or $\begin{matrix}SO''\\H'_2\end{matrix}{>}O''_2$ or $(HO)'_2SO''$.

A few are on the type of three molecules; as, $(H_2O)_3$:

Phosphoric acid,
$3H_2O$, P_2O_5 or H_3PO_4 or $\begin{matrix}PO'''\\H'_3\end{matrix}{>}O''_3$ or $(HO)'_3PO'''$.

We may also suppose these acids to be formed by the union of hydroxyl with a negative radical, as in the last formula given in each of the above.

73. These acids are all named from the negative radical. If only two acids of an element are known, the stronger equivalence is indicated by the suffix *ic*, and the weaker by *ous*. If four acids exist, the prefix *per* is placed before the higher *ic* acid, to indicate the highest combination, and the prefix *hypo* before the lower *ous* acid, to indicate the lowest. Generally these suffice: the other acids, if any, are indicated by arbitrary names.

We have the following acids of chlorine and of sulphur:

HCl	Hydrochloric acid.	H_2S	Hydrosulphuric acid.
$HClO$	Hypochlorous acid.	H_2SO_2	Hyposulphurous acid.
$HClO_2$	Chlorous acid.	H_2SO_3	Sulphurous acid.
$HClO_3$	Chloric acid.	H_2SO_4	Sulphuric acid.
$HClO_4$	Perchloric acid.		(See p. 115).

74. A salt is formed by the substitution of a metal for the hydrogen in an acid. Binary compounds like KI, KCl, NaCl are called *haloid salts*, from their resemblance to the last named, which is common salt. Their names all end in *ide*, as before described.

The salts which contain oxygen are ternary compounds, and are called *oxy-salts*. These derive their names from the acids from which they are formed, only changing *ic* to *ate*, and *ous* to *ite*, and prefixing the name of the basic element or radical. Thus:

$KClO$	Potassium hypochlorite,	or hypochlorite of potassium.
$KClO_2$	Potassium chlorite,	or chlorite of potassium.
$KClO_3$	Potassium chlorate,	or chlorate of potassium.
$KClO_4$	Potassium perchlorate,	or perchlorate of potassium.

75. Acids are said to be monobasic, bibasic, tribasic, etc., according to the number of hydrogen atoms they contain that may be replaced by a positive atom. Thus, sulphuric acid is bibasic, because it has two replaceable atoms of hydrogen. If one is replaced by a monad, an *acid* salt is formed; if both are replaced either by two monads or by one dyad, a *normal* salt is formed. For example:

$KHSO_4$	is the acid potassium sulphate (or bisulphate).
K_2SO_4	is the normal potassium sulphate.
$Pb''SO_4$	is the normal lead sulphate.
$Al_2'''(SO_4)_3$	is the normal aluminium sulphate.

76. Double salts are those in which the hydrogen atom is replaced by atoms of two different metals.

The alums are familiar examples. Thus, common alum has the following composition:

$$Al_2O_3,\ 3\,SO_3 + K_2O,\ SO_3;\ \text{or}\ Al_2K_2S_4O_{16};\ \text{or}\ AlK,\ (SO_4)_2.$$

The haloid salts also form double salts* which are ternary. The double chloride of potassium and platinum has the formula:

$$2\,KCl,\ PtCl_4,\ \text{or}\ K_2PtCl_6,\ \text{or}\ (KCl)_2,\ Cl''_2(PtCl_2).$$

77. Sulphur acts like oxygen as a linking atom, and there exists a series of sulphur compounds analogous to those already given of oxygen. Thus:

		OXYGEN ANALOGUES.
K_2S	is a basic sulpho-anhydride.	K_2O
SnS_2	is an acid sulpho-anhydride.	SnO_2
H_2S	is a sulpho-acid.	H_2O
HS	is its radical.	HO
KHS	is a sulpho-base.	KHO
H_2SnS_3	is a sulpho-acid.	H_2SnO_3
K_2S, SnS_2,	or K_2SnS_3, is a sulpho-salt.	K_2SnO_3

There are other series of less importance; we mention only that derived from hydrofluosilic acid, $2HF,\ Si,\ F_4$, in which the hydrogen may be replaced by metals; as, $2KF,\ SiF_4$ or $K_2\ SiF_6$.

78. When salts are dissolved in water, and the solution evaporated, bodies are produced which have regular or crystalline forms. These crystals are frequently found to contain a molecule of the salt and from 1 to 24 molecules of water. In such crystalline molecules the water is supposed to exist as such, and is called the *water of crystallization.* The water is an essential part of the crystalline molecule, but not of the chemical molecule.

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* Such double salts of saturated bodies are called "molecular compounds." The linking chlorine appears to act diatomic.

This is evidenced by the fact that the same saline molecule may combine with different proportions of water to form different crystalline forms. Thus sodium carbonate crystallizes from a boiling solution as $Na_2CO_3 + H_2O$, in rectangular tables; at ordinary temperatures, as, $Na_2CO_3 + 10H_2O$, in rhombic prisms. In dry air these rhombic prisms lose their water of crystallization and crumble to a white powder. This is called *efflorescence.* Some crystals require a higher temperature to expel their water of crystallization. Blue cupric sulphate is $CuSO_4 + 5H_2O$. It loses 4 molecules of water when dried at 100° C., and does not give up the remaining molecule until it is heated to 200° C. It then forms a white powder, $CuSO_4$, and is said to be *anhydrous.* The last molecule of water is sometimes called the *water of constitution,* because it seems to be more strongly connected with the saline molecule than the others; and this is indicated by separating it from them in formulæ; thus, $H_2O, CuSO_4 + 4H_2O$.

79. The notation of compounds is their representation by means of symbols and signs. From what has already been said, it is evident that this will vary with the ideas which are intended to be conveyed. As a general rule, the positive atoms and radicals are written first. A numeral placed below a symbol multiplies it alone. A numeral placed in any other position multiplies every atom by itself until some sign of separation, as a bracket, parenthesis, or comma, is reached.

In mineral chemistry, the dualistic formulæ are of advantage when we wish to express that the same anhydride is common to several compounds; as, K_2O, CrO_3, and $K_2O, 2CrO_3$ instead of K_2CrO_4 and K_2Cr2O_7. In organic chemistry, the formulæ are generally structural. We contrast these systems by the following equations.

The reactions between lead nitrate and sulphuric acid:

EMPIRICAL. $PbN_2O_6+H_2SO_4=\underset{\vee}{PbSO_4}+H_2N_2O_6.$

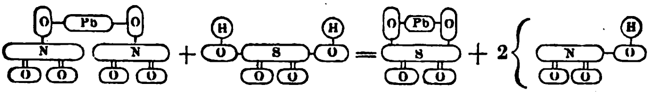
DUALISTIC. $PbO,\ N_2O_5+H_2O,\ SO_3=\underset{\vee}{PbO,\ SO_3}+H_2O,\ N_2O_5.$

TYPICAL. $$\left.\begin{matrix}(NO_2)_2\\Pb\end{matrix}\right\}O_2+\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2=\underset{\vee}{\left.\begin{matrix}SO_2\\Pb\end{matrix}\right\}}O_2+2\left(\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O\right).$$

STRUCTURAL.

$$Pb{<}\begin{matrix}O\text{-}NO_2\\O\text{-}NO_2\end{matrix}+\begin{matrix}HO\\HO\end{matrix}{>}SO_2=Pb{<}\underset{\vee}{\begin{matrix}O\\O\end{matrix}}{>}SO_2+2(HO\text{-}NO_2).$$

GLYPTIC.



NOTE.—The student will find it of great advantage to be enabled to use readily all systems of formulæ. In this book, although preference is given to structural formulæ, the dualistic system is still retained.

In many of the older text-books on chemistry, different atomic weights were assigned to the elements, giving rise to a different set of formulæ.

Recapitulation.

Atoms differ in—

Weight — measured relatively by the hydrogen unit.
In electrical relations — positive or negative.

In combining power
- perissads, odd
  - monads ′ or univalent; as, H'.
  - triads ‴ or trivalent; as, B'''.
  - pentads ^{V} or quinquivalent; as, N^{V}.
  - heptads ^{VII} or septivalent; as, F^{VII}.
- artiads, even.
  - dyads ″ or divalent; as, O''.
  - tetrads ^{IV} or quadrivalent; as, C^{IV}.
  - hexads ^{VI} or sexivalent; as, S^{VI}.

Molecules are
- composed of like atoms — elementary; as, H_2.
- composed of unlike atoms — compound; as, HCl.

Radicals are residues of molecules, and act as atoms.

They are
- either an elementary atom, as H,
- or an unsaturated molecule, as HO.

Saturated compounds are classified

- binary oxides
  - basic anhydrides; as, K_2O.
  - acid anhydrides; as, SO_3.
  - neutral bodies; as, MnO_2, H_2O.
- basic hydrates; as, KHO.
- acids . . .
  - binary or haloid acids; as, HCl.
  - ternary acids; as, H_2SO_4.
- salts . . .
  - binary or haloid salts; as, KCl.
  - ternary salts; as, K_2SO_4.
  - double salts; as, $KAl(SO_4)_2$.

The *actual* proportion of atoms in a compound is always denoted by numerals; as, HCl, H_2O, Hg_2Cl_2, $HgCl_2$, which take the names, *prot*, 1; *bi*, 2; *ter*, 3; *tetra*, 4; *penta*, 5; *sesqui*, 2 : 3.

The *relative* proportion of atoms in the compounds of a given element, as R, is denoted by prefixes and suffixes.

The highest equivalence of four compounds by *per*—R—*ic*.
" " " " two " " R—*ic*.
The lowest " " two " " R—*ous*.
" " " " four " " *hypo*—R—*ous*.

The termination *ide* is applied only to binaries; as, KCl.

The terminations of ternary salts are:

ite, when the acid ends in *ous;* as, K_2SO_3.
ate, " " " " " *ic;* as, K_2SO_4.

The termination of compound radicals is *yl;* as, HO.

CHAPTER IV.

WATER AND ITS ELEMENTS.

ELEMENT.	SYMBOL.	WT. OF ONE LITRE IN GRAMMES.	SPECIFIC GRAVITY.		ATOMIC WEIGHT.	DISCOVERER.
			AIR = 1.	H = 1.		
Hydrogen . .	H	.0896	.0692	1.	1	Cavendish, 1766.
Oxygen	O	1.4336	1.1056	16.	16	Priestley, 1774.
Water, Steam	H_2O	.8064	.622	9.		Investigated by Lavoisier, 1781.
Water, Liquid	H_2O	1000.	773.	11160.		

80. We have already learned that water is composed of hydrogen and oxygen, in the proportions of two volumes of hydrogen to one of oxygen, or, by weight, of 2 parts of hydrogen to 16 of oxygen.

HYDROGEN.

81. Hydrogen is an essential constituent of water, of acids, and of most organic compounds.

It may be obtained from any of these bodies. From water, (1) by the electrical current (Art. **47**); (2) by passing steam over iron filings heated to redness (Exp. 29); (3) from cold water by the action of sodium (Exp. 4); (4) by placing bright zinc strips in water. In this case the zinc decomposes the water, forming zinc oxide and setting the hydrogen free: $Zn + H_2O = ZnO + H_2$. The action soon ceases, because the zinc becomes coated with an insoluble film of the oxide, which prevents further oxidation.

(5) If, however, the water is mixed with one-fifth of its weight of sulphuric acid, the action is continuous,

because the acid unites with the oxide as fast as it is formed to produce zinc sulphate, ZnO, SO_3, which readily dissolves in the excess of water, and thereby the surface of the zinc is kept bright and clean. We may suppose that the two reactions occur simultaneously, and that the molecule of water decomposed is that previously in combination with the acid, and may represent the process by a single equation:

$$Zn + H_2O, SO_3 = ZnO, SO_3 + H_2.$$

If too little water is present, a sulphate is produced which is with difficulty soluble, and the action is less energetic.

82. A convenient apparatus is shown in Fig. 20: a represents a flask containing a handful of granulated zinc;* b is a funnel reaching almost to the bottom of the flask, through which the acidulated water may be poured as required; and c is a tube just passing through the cork for the escape of the gas. The end of the tube, d, may be placed under a receiver, as the cylinder e. The cylinder is first to be filled with water and inverted in a suitable cistern also containing water. As the hydrogen, at first, is mixed with the air of the flask, none of the escaping gas should be employed in experiments *until the air has been thoroughly expelled from the apparatus.* The moment when this result is reached may be ascertained by filling test tubes with the escaping gas in the water cistern, and, after lifting them carefully from the water without changing their vertical position, applying a lighted match to the mouth of the tube. If the hydrogen is free from air, it will burn quietly; but if much air is present, the mixture will be ignited with a sharp explosion.

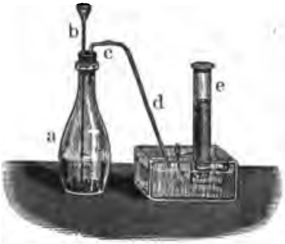


FIG. 20.

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* Zinc is granulated by melting zinc scraps in an iron ladle, and slowly pouring the molten metal from a height into a pail filled with cold water.

Note.—When explosions are anticipated in the process of experiment, the quantities operated on should be small; and, in the case of gases, the vessels in which they are contained should be of thick glass. Even in this case, it is prudent to wrap glass vessels in a thick towel before applying the match.

The hydrogen obtained from zinc is liable to certain impurities, which may be sufficiently removed by passing the gas through three bottles containing, respectively, (1) a dilute solution of sodium hydrate, (2) a dilute solution of silver nitrate, and (3) small lumps of charcoal. A fourth wash bottle, containing strong sulphuric acid, may also be used to dry the gas.

The dry gas may be collected over quicksilver, or used in experiments which require only a stream of the gas. The fourth bottle is unnecessary when the hydrogen is collected over water.

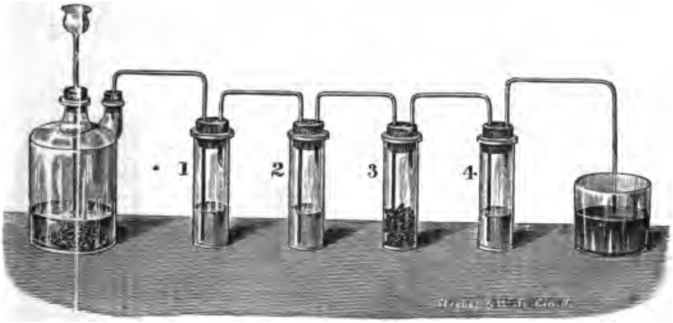

Fig. 21.

83. Physical properties of hydrogen. Hydrogen is a colorless, odorless, and tasteless gas, which liquifies under a pressure of 280 atmospheres. It is found convenient to assume it as a standard for the specific gravity of aëriform bodies. It is 14.43 times lighter than air. The cold produced by the sudden expansion of this liquid is sufficient to reduce a portion to a fine spray containing solid particles.

Exp. 62.—Prepare a solution of soap, and, by means of a tobacco pipe connected with the evolution tube, inflate soap bubbles with hydrogen. When detached from the pipe they rise rapidly, showing that *hydrogen is lighter than air.* Small bags made of caoutchouc and filled with the gas will rise like a balloon.

Owing to its lightness, jars may be filled with the gas by *displacement*.

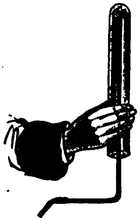

FIG. 22.

Exp. 63.—This may be done by fitting a vertical tube to a flask from which the gas is escaping rapidly, and by holding over this a dry cylinder (Fig. 22). After a few minutes, the hydrogen will be found to have so completely displaced the air of the cylinder that no explosion will ensue when a lighted taper is applied to the mouth of the cylinder.

Exp. 64.—So, also, hydrogen may be poured from one cylinder to another (Fig. 23), if we only remember that in pouring hydrogen the gas will flow *up*, and not down as is the case in pouring water. Unless the receiving cylinder is much smaller than the other, all its air will not be displaced, and now an explosion may be expected when a lighted taper is applied at its mouth.

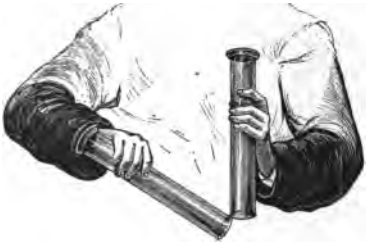

FIG. 23.

84. Hydrogen is taken as the unit of atomic weights. Its rate of diffusion is the highest known. This is due to its high rate of molecular motion. (See note to p. 52). It diffuses 3.8 times faster than air.

Exp. 65.—Close the mouth of a glass funnel having a long delivery tube by a septum of plaster of Paris. This may be done by making a moderately thick paste of the plaster with water on a plate, inverting the mouth of the funnel therein, then suffering the plaster to harden and to dry thoroughly. Detach the funnel from the plate, and place the open tube in colored water, inverting over the closed mouth a jar filled with hydrogen. The hydrogen diffuses into the funnel faster than the air diffuses out, and soon bubbles of gas escape through the water. Now remove the jar, and the hydrogen will escape in the contrary direction, leaving a partial vacuum in the funnel, which becomes manifest by the rise of water in the tube.

A beautiful modification of this is shown in Fig. 24. A large diffusion tube is attached to a two-necked flask, which has a tube extending through the second neck below the surface of some water contained in the flask. If the septum is dry and the fittings are air-tight, a fountain of water will be formed of considerable height.

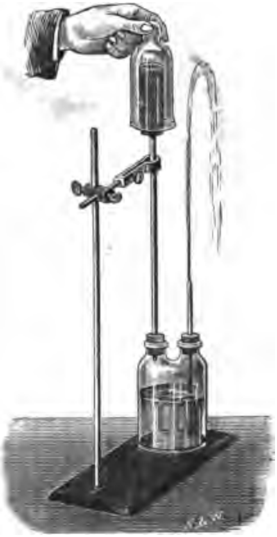

FIG. 24.

Exp. 66.—A curious experiment which shows that sound is much enfeebled in hydrogen may be performed by filling the lungs of the experimenter with *pure* hydrogen and his then attempting to speak. The voice will be weak and piping.

85. Chemical properties.

The following experiments illustrate some of the chemical properties of hydrogen.

Exp. 67.—Fill a cylinder with dry hydrogen, and introduce into this a lighted wax taper. (Fig. 25.) The gas will be enkindled at the mouth of the cylinder. If the taper is pushed up into the cylinder, its flame will be extinguished. On withdrawing the taper, it may be again ignited by the burning gas, then again extinguished by passing it upward into the gas, and then rekindled for several times in succession.

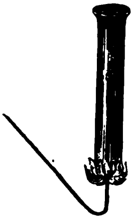

FIG. 25.

This shows that hydrogen burns when in contact with the air, but that it does not support ordinary combustion.

Exp. 68.—Attach to the drying bottle a vertical tube drawn out so as to yield a small jet, as in Fig. 26. If the jet of gas be ignited, it will burn with an almost non-luminous flame. Hold over this flame an evaporating dish containing ice. The outside of the dish will become covered with moisture, and in a short time will yield drops of water.

This experiment may be modified by burning the jet within a wide glass tube. The upper part of the tube will be covered with condensed water. At the same time, a musical note will be produced, which will vary in pitch as the tube is raised or lowered. The sound is due to a series of small explosions in rapid succession, which produce regular vibrations in the air column of the tube.

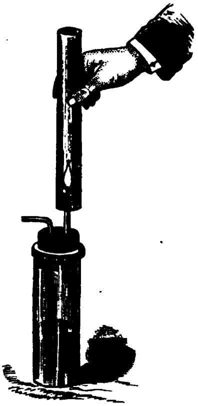
FIG. 26.

86. The product of the combustion of hydrogen in air is water. From this fact the gas derives its name. The reason why the flame is so feebly luminous is that neither the particles of the gas nor of the steam which is formed become incandescent. The flame is nevertheless very hot.

Exp. 69.—Hold in the flame a solid body, as a thin platinum wire or a bit of chalk sharpened to a point. The solid particles will soon become white hot, and the flame increase perceptibly in illuminating power.

The heat evolved by the combustion of one gramme of hydrogen is 34462 thermal units. The temperature attained, under favorable conditions, is very nearly 2800° C.

87. Hydrogen is a powerful reducing agent.

Exp. 70.—If the dry gas be passed through a tube containing cupric oxide kept at a low red heat, metallic copper will be produced. (Fig. 27.) The oxygen previously combined with the copper unites with the hydrogen to form steam. (See Exp. 30).

88. Hydrogen acts energetically in what is known as the *nascent state;* that is, at the moment that it is set free, and before it becomes perceptible to the eye.

Exp. 71.—Place in a beaker a strip of zinc; place upon this silver chloride (Exp. 57), and cover both with very dilute hydrochloric acid. In a few hours the silver will be reduced to the metallic state through the union of its chlorine with the hydrogen set free by the action of the acid upon the zinc.

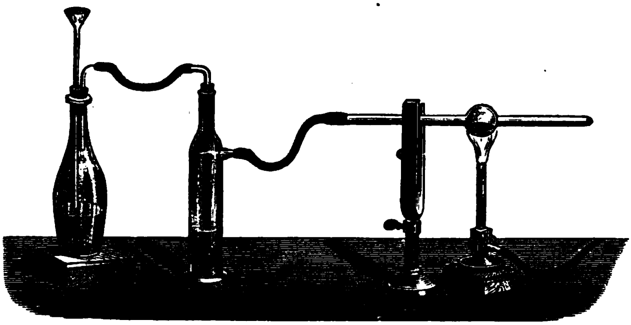

FIG. 27.

89. Hydrogen is absorbed, or "occluded," by many metals in large quantities. Palladium absorbs 200 times its volume of hydrogen, and forms a substance which is apparently an alloy. For this reason Graham inferred that hydrogen is a metal.

TESTS.—Hydrogen may be recognized by its physical properties and by its combustibility, but more certainly by the fact that two volumes of the gas mixed with one volume of oxygen, and exploded, form water.

90. Physiological properties. Although the lungs may be filled once with pure hydrogen without danger, it does not support respiration. Small animals confined in it speedily die.

91. The only uses which have been made of hydrogen are: (1) as a source of heat in melting platinum and other refractory metals; (2) to render the calcium employed in the Drummond light highly incandescent; and (3) as a material for filling balloons.

OXYGEN.

92. Oxygen is found uncombined in the air, and is a constituent of water, of most minerals, and of many organic bodies, like sugar, starch, and alcohol.

It may be obtained, (1) by the electrolysis of water (Art. **47**), and (2) by heating many of the higher oxides, as, HgO, MnO_2, Pb_3O_4, I_2O_5. (See §§ **413, 507**).

It is most conveniently prepared by heating potassium chlorate, $KClO_3$. One gramme of this salt yields 273.8 cubic centimetres of oxygen, and a residue of 6 decigrammes of potassium chloride, $KClO_3 = KCl + 3\overset{\frown}{O}$. At a gentle heat, one-third of the oxygen is given off—$2KClO_3 = KClO_4 + KCl + \overset{\frown}{O}_2$—and potassium perchlorate is formed. This body at a higher temperature also decomposes and yields the remaining oxygen—$KClO_4 = KCl + \overset{\frown}{O}_4$—but the gas is evolved so rapidly that considerable dexterity is required in manipulation. Where large quantities are required, it is better to use a mixture of equal parts of manganese dioxide and potassium chlorate. The reaction is the same as before. The manganese dioxide is not decomposed, but by its presence regulates the action, and the mixture requires less heat than the chlorate alone.*

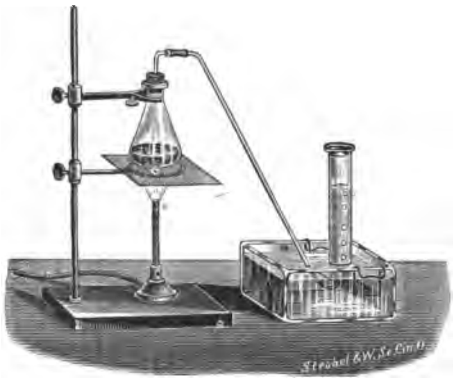

FIG. 28.

The process may be conducted in a stout glass flask, as shown in Fig. 28. A retort of iron or copper is very convenient.

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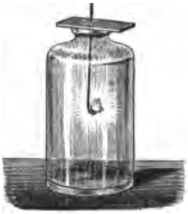
* It is advisable to heat the manganese dioxide to redness, and then cool it before using, because, if it contains carbon, explosive compounds are sometimes formed.

93. Physical properties. Oxygen may be collected over water, as 100 volumes of water, at 15° C., absorb but 3 of this gas. It is colorless, odorless, and tasteless, and has recently been liquefied under a pressure of 320 atmospheres.

94. Chemical properties. Oxygen forms compounds with all of the elements except fluorine. We have seen that ordinary combustion is due to the union of bodies with oxygen. Any substance which will burn in air will burn far more brilliantly in pure oxygen; others, that are generally considered incombustible, burn with violence in oxygen.

Exp. 72.—Having lighted a small taper, blow it out so as to leave a small spark on the wick. Plunge this into a jar of oxygen. It will be immediately rekindled. It may then be again blown out and rekindled so long as the gas remains.

Exp. 73.—Place a little sulphur in a deflagrating spoon; kindle this in the flame of a lamp and plunge it into a jar of oxygen. The sulphur will burn with a lilac flame.


FIG, 29.

Exp. 74.—Repeat the last experiment with a small piece of dry phosphorus,* and ignite it by a hot wire. On plunging it into the oxygen, it will burn with dazzling brilliancy.

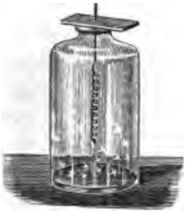


FIG. 30.

Exp. 75.—Coil an iron wire into the form of a spiral by winding it around a pencil. Pass one end through a cork which fits the mouth of the jars used, and tip the other with melted sulphur or tinder. Set fire to the tinder and plunge the wire into a jar of the gas. The iron will take fire and burn, throwing out bright sparks.

Steel gives more brilliant effects. A broken watch spring, straightened by heating so as to destroy its temper, may be used instead of the iron wire.

These experiments may be extended by using, (1) on the spoon, a pellet of napthalene or of potassium; (2) attached to a wire, a bit of charcoal, or strips of zinc, thin copper, etc. Magnesium wire burns brilliantly even in ordinary air.

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* Phosphorus should neither be handled nor cut except under water.

The experiments may be modified by using, instead of jars filled with oxygen, a stream of the gas. If the student does not possess a suitable gas holder, he may use large ox bladders softened in water and then well rubbed with glycerine. These bladders are to be tightly fitted with a glass tube, the air pressed out, and then inflated with oxygen. A temporary stopper for the tube may be made by slipping over the end a bit of rubber tubing, and plugging up the open end of the rubber tube with a glass rod.

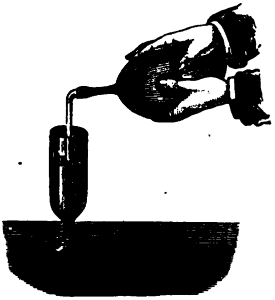

FIG. 31.

Exp. 76.—Place a pellet of phosphorus in a conical wine-glass, and pour enough hot water over the phosphorus to melt it. Now force a stream of oxygen on the melted phosphorus. It will burn under the water.

Exp. 77.—Arrange a combustion tube as shown in Fig. 32. Place in one end of the tube a bit of sulphur, or of coal, or of potassium, etc., and connect with the other end tubes plunged in empty jars to collect such products as may be volatile. Now force a stream of the gas, dried by passing it through sulphuric acid, through the tube, and ignite the bodies placed in it by heating them with the flame of a lamp. They will burn brilliantly, as in the former cases.

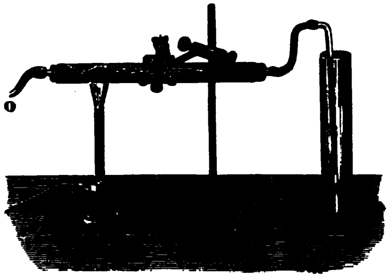

FIG. 32.

95. The products of the combustion should be tested. If a little water be poured into the jars and shaken up, the charcoal jar will be found to contain carbonic acid; the sulphur, sulphurous acid; the phosphorus, phosphoric acid. These solutions will each redden blue litmus. The potassium residue, moistened with water, will change red litmus to blue. It is alkaline.

96. Tests for free oxygen. When oxygen is not much diluted with other gases, it may be tested by plunging into the jar containing it a splinter of pine tipped with a glowing coal. If the coal bursts into a flame, the gas is either oxygen or nitrous oxide.

Oxygen is not absorbed by potassium hydrate, but if potassium hydrate is mixed with pyrogallic acid, the alkaline pyrogallate which is formed rapidly absorbs oxygen and becomes black. This is not only a valuable test for free oxygen, but it may be used to absorb oxygen from gaseous mixtures.

Exp. 78.—Take a long tube closed at one end, and pour into it a spoonful of a solution of potassium hydrate. Now drop into the tube a few flakes of pyrogallic acid. Close the tube with the thumb, and, after shaking, invert it in a dish of water The pyrogallate will be blackened, and, on removing the thumb, the water will rise in the tube, because the oxygen has been absorbed from the air contained within it.

97 Physiological properties. If a small animal be confined in a jar of oxygen, its respiration becomes increased; it becomes feverish and soon dies, because of the too great supply of oxygen. Diluted with nitrogen, it is essential to the respiration of all animals.

Exp. 79.—Shake up a little fresh venous blood in a jar of oxygen; it will quickly become changed to red, or arterial, blood. This is the change which goes on continually in our lungs.

98. Uses of oxygen. We have already seen that oxygen is an active agent in promoting chemical changes in the laboratory of the chemist and in the greater workshop of Nature. The processes of respiration, of ordinary combustion, of fermentation, and of decay are all dependent upon it.

99. Since these various processes of oxidation consume oxygen, it may be supposed that the time might come in which the atmosphere would no longer contain it, and, therefore, that respiration would become impossible and animal life cease. Lehmann has calculated that the air contains enough oxygen to last 800,000 years; but the agencies of nature so balance each other that the proportions of the atmosphere remain unchanged.

The principal products of combustion and respiration are carbonic anhydride and water. These are necessary to the growth of plants. They consume them to form the materials which we use for food and fuel. The green parts of the plants evolve, in the sunlight, the oxygen required for animal life.

Exp. 80.—Place a handful of fresh green leaves in a bell glass. Fill this completely with water, and invert on a plate also containing water. Now expose the leaves to the bright sunlight for several hours. Bubbles of gas will collect in the upper portion of the glass, which on examination will prove to be *oxygen.*

100. The oxy-hydrogen blowpipe is one of the most efficient artificial sources of heat and light. This is an apparatus so contrived that two volumes of hydrogen are burned with one volume of oxygen. It is exceedingly dangerous to ignite large quantities of these gases previously mixed; hence, a double jet is used, as shown in Fig. 33.

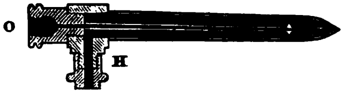

FIG. 33.

The interior jet, O, supplies a stream of oxygen, and the outer jet, H, a stream of hydrogen. The hydrogen is first turned on and enkindled; the oxygen is then forced through the hydrogen flame, and the two gases burn at the moment of mixing.

If both gases are pure and dry, the flame is feebly luminous, but intensely hot. Strips of iron, copper, zinc, etc., burn with great brilliancy in it. Metals like antimony and arsenic are exposed to its action by supporting them on bits of charcoal. All the metals, without exception, are melted by it. By directing this jet into the interior of a small furnace lined with lime, Deville has succeeded in melting 100 kilogrammes of platinum at a single charge.

If the jet be directed on the stem of a clay tobacco pipe, it fuses. Lime does not fuse in the jet, but becomes so highly incandescent as to yield a very pure white light of dazzling brilliancy. This, properly mounted in the focus of a concave mirror, has been used for signalling, under the name of the Drummond, or calcium, light. It has been seen at a distance of more than 100 miles.

Exp. 81.—Inflate soap bubbles with a mixture of two volumes of hydrogen and one of oxygen. *After* they have risen from the jet, apply a lighted taper. A bubble the size of a tumbler will explode with a loud report.

Such mixtures of oxygen or of air with hydrogen or illuminating gas, or with the vapors of coal oils, are dangerously explosive.

101. Ozone. Whenever an electrical machine is in operation, a pungent odor is developed in the air through which the sparks pass. The same odor is perceived when a clean stick of moistened phosphorus is allowed to remain for two hours in a large flask loosely stoppered. In both cases the odor is due to a change effected in the oxygen of the air, by which it becomes remarkably energetic. This modification of oxygen is called *ozone.* Ozone may also be prepared by shaking a little ether in a jar so as to fill it with vapor, and then plunging a heated glass rod into the jar.

No method has been devised of obtaining ozone pure. It is always mixed with common oxygen, but has been obtained by induced electricity in as great a proportion as 15 per cent. Even two per cent will suffice to exhibit its wonderful properties.

102. Physical properties. Ozone is condensed oxygen. It is re-converted by heat into ordinary oxygen with a permanent increase of volume. Its specific gravity is probably 1½ times that of oxygen: hence, a molecule of ozone contains three atoms of oxygen, while the molecule of ordinary oxygen contains two atoms.*

103. Chemical properties. Ozone is the most energetic oxidizer known. Even in the dilute state it is capable of bleaching indigo, oxidizing silver and other metals, and displacing hydrogen from its compounds with sulphur and iodine. Caoutchouc and other organic substances are quickly corroded by it.

TESTS.—When ozone acts upon potassium iodide, potassium oxide is formed and iodine is liberated.† Hence, we may use this reaction in two ways as a test for ozone.

Exp. 82.—(1) Moisten red litmus paper with a solution of potassium iodide; when the potassium oxide is formed by the ozone, it colors the paper blue. (2) Moisten unsized paper with a dilute solution of potassium iodide, containing a little boiled starch. The iodine set free by the ozone colors the starch blue. If much ozone is present, the iodine changes to iodic acid, I_2O_5, and the paper is again bleached.

104. Ozone is frequently found in the atmosphere. This ozone is probably produced by the processes of oxidation which are every-where going on in nature. The slow oxidation of turpentine and of many ethereal oils is attended by the production of ozone, especially if these bodies are exposed to the sunlight.

105. Uses. The bleaching power of the air is due to the ozone which it contains. The atmospheric ozone destroys the malarious exhalations which arise from decaying animal and vegetable matters. It is difficult to over-rate its usefulness as a disinfecting agent.

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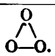
* Oxygen, O=O; Ozone, .

† $2KI + O = K_2O + \underset{\smile}{2I}$. $K_2O + H_2O = 2KHO$.

It has been noticed that when the air is charged with ozone, epidemic diseases, like cholera, have abated. Conversely, air highly charged with ozone is irrespirable. It attacks the organs of respiration and produces coughing; hence it is supposed to assist in producing epidemics of catarrh and influenza.

106. Antozone. Some suppose that whenever ozone is formed, another modification of oxygen is also produced. This is called *antozone.* Its molecule contains but one atom. The white clouds which are formed when ozone is liberated in the presence of water are supposed to be due to the peculiar property which antozone has of forming clouds or mists with water. The existence of antozone is, however, still questioned.

107. Oxygen has at least two modifications, ordinary oxygen and ozone. Although these have different properties, one may be converted into the other without loss of weight. Several other elements occur in different states. These different states are said to be *allotropic* forms of the element; the word allotropy signifying *of a different character.*

WATER OR HYDROGEN OXIDE, H_2O.

108. Water is seldom found pure. The rain that falls in open fields near the end of a long shower is very nearly pure water. Although the great part of the water of our globe occurs in its free state, it enters largely into mineral combinations, and is, besides, essential to vegetable and animal structures.

109. We have shown that water is formed by the union of oxygen with hydrogen. It is one of the products formed when an organic substance containing hydrogen is burned in air. It is prepared sufficiently pure for practical purposes by the distillation of ordinary water.

Fig. 34 represents an apparatus that may be used for this purpose. A is a capacious flask in which rain or well water is boiled: the escaping steam is cooled by passing through a *condenser*, B.

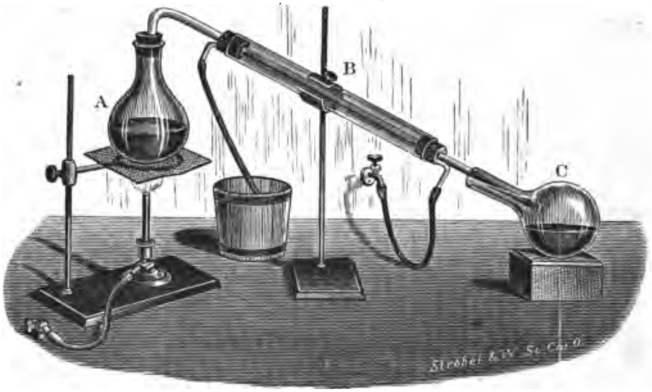

A
B
C
Strobel & W. Sc. Cin. O.

FIG. 34.

The form in the figure is known as Liebig's condenser. It is kept constantly cool by a stream of cold water entering at the bottom and flowing out at the top. The product of the distillation, which is called the *distillate*, is collected in the receiver, C. The first portions of the distillate are thrown away, and the process is stopped when about four-fifths of the water has passed over.

110. Physical properties. At ordinary temperatures, water is a tasteless, odorless liquid. When seen through a depth of several yards, it has a bluish color. It is assumed as the standard for specific heat. One cubic centimetre (Fig. 35) of distilled water at 4.1° C., its point of greatest density, is taken as the unit of weight in the metrical system. This unit is called one gramme = 15.4 grains. At this temperature it is taken as the standard of specific gravity for solids and liquids.

The freezing and boiling points of water, under the pressure of one atmosphere, are taken as standards of temperature. Water freezes to ice at a temperature of 0° C., and increases about one-tenth in volume. It evaporates at all temperatures, and so rapidly at 100° C. that it is said to boil. Steam at 100° C. occupies 1696 times the volume of the water from which it was formed.

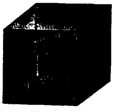


FIG. 35.

111. Chemical properties. When certain crystals are heated they give off water. The water in them appears to have one of two functions: (1) If it is easily expelled by heat, it forms part of the physical molecule, and is called the *water of crystallization;* (2) if it requires considerable heat to expel it, it forms part of the chemical molecule, and is called the *water of constitution.*

Thus, when ferrous sulphate is heated to 114° C., six molecules of the water of crystallization are driven off. On heating to 280° C., another molecule of water is driven off, which is the water of constitution. To express these different functions, we may write the formula of ferrous sulphate, $H_2O, FeO, SO_3 + 6\,H_2O$.

Some anhydrides, as K_2O or SO_3, so firmly unite with water, that heat alone will not again separate them: $K_2O + H_2O = 2KHO$; $SO_3 + H_2O = H_2SO_4$. These bodies are collectively spoken of as *hydrates*, and it seems probable that they contain water, not as such, but as the radical hydroxyl, $K\text{–}HO$; $(HO)'_2(SO_2)''$. However, some hydrates are easily decomposed by heat, as $Cu(HO)_2$, which changes to $CuO + H_2O$.

Many organic bodies, like starch, $C_6H_{10}O_5$, contain hydrogen and oxygen in the same proportions as they are found in water, and for this reason have been called *carbo-hydrates.* Nevertheless, it has not been proved that the formula of starch could be correctly written $C_6(H_2O)_5$, or that water, as such, enters into its molecule. Bodies that contain neither water nor hydroxyl are said to be *anhydrous.*

112. Water is specially useful to the chemist as a solvent. It dissolves a large number of bodies, and, on being evaporated, again yields them unchanged. The rain, in falling, absorbs many atmospheric constituents, and afterward, sinking into the ground, dissolves the soluble matters of the soil. If this water again comes to the surface, as spring or river water, it contains more or less solid matters, varying with the nature of the rocks through which the water flows. The ocean and isolated seas, like the Caspian, are the final reservoirs of rivers. Their waters undergo a natural distillation, yielding pure water to the clouds, and become, in consequence, more highly charged with saline matters, or become salt water. The water of the Great Salt Lake contains 12,000 grains of solid matter to the gallon. Sea water averages about 2,000 grains to the gallon. The potable waters of springs and rivers seldom contain as high as 100 grains to the gallon, and many lakes and rivers in granitic regions are very nearly pure.

113. The healthfulness of potable waters is not so much dependent on their mineral as upon their organic constituents. If water contains ten grains to the gallon of organic matters in a state of decomposition, it is likely to be very unhealthful. Running waters are self-purifying, because their organic impurities are continually exposed to the air and are entirely decomposed. Water may be purified for drinking purposes by filtering through a thick layer of charcoal.

Distilled water is unpalatable, or "flat." The palatableness of water depends largely on its gaseous constituents. If distilled or boiled water is suffered to trickle through the air, it becomes "aërated" and more pleasant to the taste.

Tests.—When obtainable in large quantities, water is sufficiently known by its physical properties. The presence of water in mixtures is indicated by its power of changing white anhydrous cupric sulphate to a blue color. The anhydrous cupric sulphate, $CuSO_4$, is easily formed by gently roasting "blue vitriol."

114. Hydrogen peroxide, H_2O_2, is prepared by treating barium peroxide with dilute hydrochloric acid:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

In its concentrated form it is a syrupy liquid, having a specific gravity of 1.452. It is easily decomposed into water and oxygen. It possesses remarkable oxidizing powers, changing black lead sulphide into white lead sulphate, and decomposing potassium iodide, like ozone. Hence, this reaction may also be used as a test for hydrogen peroxide. Still more remarkable is the property which it has of inducing other peroxides, when mixed with it, to yield a part of their oxygen, both bodies becoming reduced at the same moment. Thus, when hydrogen peroxide is poured upon manganese dioxide, both bodies evolve oxygen:

$$MnO_2 + H_2O_2 = MnO + H_2O + \overset{\frown}{O}_2.$$

Recapitulation.

Hydrogen is the lightest of the elements. It is taken as the standard unit:
(1) For the specific gravity of gases.
(2) For atomic and molecular weights.
(3) For molecular volumes.
(4) For atomicity, or unit of combining power.

The basicity of an acid is the amount of hydrogen it contains that may be replaced by a metal.

Hydrogen also seems to stand midway between the metals and the other elements.

Oxygen is the most abundant element, and is strongly electro-negative.

Its compounds are:
Basic, with most of the electro-positive elements.
Acid, with most of the electro-negative elements.
Indifferent, with metallic peroxides and H_2O.

Water is proved to have the formula H_2O, both by analysis and synthesis. (Arts. **46** and **47**).

It is an indifferent body, acting—

Basic, with negative anhydrides; as, H_2O, SO_3.
Acid, with positive anhydrides; as, K_2O, H_2O.

In compounds, it may be regarded as present—

(1) As water of crystallization, $Na_2B_2O_7 + 10\,H_2O$.
(2) As water of constitution, $H_2O, FeSO_4 + 6\,H_2O$.
(3) Represented by its radical hydroxyl; as, $K\text{–}HO$; $(HO)_2(SO_2)''$.

CHAPTER V.

THE CHLORINE GROUP (HALOGENS).

ELEMENT.	STATE AT 15° C.	SYMBOL.	SPECIFIC GRAVITY. $H_2O = 1$.	IN AËRIFORM STATE. SPECIFIC GRAVITY.		ATOMIC WEIGHT.	DISCOVERER.
				AIR = 1.	H = 1.		
Fluorine	Gas	F		1.31?	19?	19.	
Chlorine	Gas	Cl	1.33	2.47	35.5	35.5	Scheele, 1774.
Bromine	Liquid	Br	2.96	5.54	80	80	Balard, 1826.
Iodine	Solid	I	4.95	8.79	127	127	Courtois, 1812.

115. These four elements compose a natural group, the members of which exhibit a gradation of similar properties. They are all found in minute quantities in sea water and in many mineral springs. They are frequently called the *halogens* (ἅλς, the sea), because they form binary compounds resembling sea salt; as, NaF, NaCl, NaBr, NaI. Such compounds are called the *haloid salts.* So, also, each of these elements combines with an equal volume of hydrogen to form an acid which is called a *haloid acid.* These acids are HF, hydrofluoric; HCl, hydrochloric; HBr, hydrobromic; HI, hydriodic. The haloid acids are gases distinguished by a great attraction for water, and readily forming with it solutions which act as the free acids would act. In these compounds they are monads; but they seem also to act as triads, pentads, and even as septads. The halogens are never found native, and it is doubtful whether fluorine has ever been isolated.

The last three are liberated in the aëriform state by heating their haloid salts with a mixture of manganese dioxide and sulphuric acid. The general reaction may be expressed by the equation for chlorine:

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + 2Cl.$$

Their chemical energies are very active. The general order of their affinities for the positive elements is inversely as their atomic weights; their affinities for oxygen increase with their atomic weights. Fluorine is probably an incoercible gas; chlorine is a yellowish gas, liquefying at —40° C.; bromine, a red liquid, boiling at 63° C.; and iodine, a black solid, melting at 115° C. and boiling at 200° C.

FLUORINE.

116. The most abundant compound of fluorine is fluor spar (CaF_2). It is also found in cryolite ($3NaF, AlF_3$), in many other minerals, and in the bones and the teeth.

117. The chemical properties of fluorine are probably analogous to those of chlorine. It forms no compounds with oxygen, nor with any others of the non-metals except hydrogen, boron, and silicon.

118. Hydrofluoric acid, HF. This acid is liberated in the gaseous state when powdered fluor spar is treated with twice its weight of strong sulphuric acid:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

Anhydrous hydrofluoric acid is a colorless, volatile liquid which boils at 19.4° C., and emits dense fumes at ordinary temperatures. Both the gas and the liquid are readily soluble in water. The commercial acid of sp. gr. 1.15 has the formula $HF, 2H_2O$.

The acid powerfully corrodes the skin, a single drop producing a painful sore, and the fumes are dangerously irritating to the lungs. The most useful property which it possesses is its power of combining with silicon to form the gaseous fluoride of silicon (SiF_4). Glass is made of various silicates, as silicate of soda and silicate of lime; hence, hydrofluoric acid is used for etching glass.

Exp. 83.—Coat a glass plate with a thin layer of wax, and then, by means of a sharp point, engrave a word or drawing so that its lines shall expose the glass. Place the waxed surface over a leaden dish containing a mixture of fluor spar and sulphuric acid. Warm the dish gently, taking care not to melt the wax. In a few hours the glass will be etched by the gas. The liquid $HF, 2H_2O$ may also be used for etching glass. The white crust which generally forms when the glass is etched by gaseous HF is silica. This comes from the decomposition of the SiF_4 by the water which is obtained from the sulphuric acid.

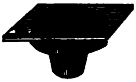


FIG. 35.

$$SiF_4 + H_2O = SiO_2 + 4HF.$$

119. The 4 HF thus liberated combines with a second portion of SiF_4 to form $2HF, SiF_4$, hydro-fluo-silicic acid, which does not corrode glass. Hydro-fluo-silicic acid forms difficultly soluble salts with potassium ($2KF, SiF_4$) and some other metals, and is sometimes used to separate these elements from their soluble compounds.

Exp. 84.—Mix 5 grammes of fluor spar with an equal quantity of powdered glass or clean sand. Put the mixture into a Florence flask furnished with a wide tube dipping into mercury in the receiver, and add 30 grammes of strong sulphuric acid. A gentle heat evolves

SiF_4. Now pour water above the mercury so carefully that none shall enter the tube. As the SiF_4 passes through the water it is decomposed, bubbles coated with an envelope of silica, SiO_2, form, and $2HF, SiF_4$ remains in solution. The silica may be filtered off through linen, and the solution of hydro-fluo-silicic acid preserved for future use.

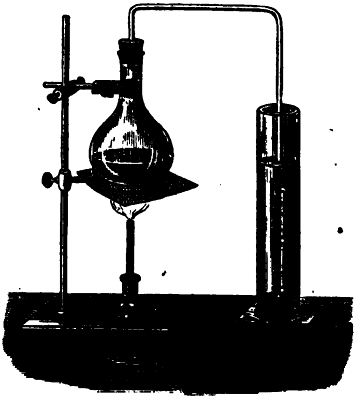


FIG. 36.

CHLORINE.

120. Chlorine is a constituent of sodium chloride (common salt) and of potassium chloride, both of which are very abundant.

121. Preparation. Chlorine may be conveniently prepared by gently heating manganese dioxide with hydrochloric acid.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

To obtain one litre of chlorine, about 20 grammes of the acid and 6 grammes of the dioxide are required.

The funnel tube shown in Fig. 37 answers for the introduction of the acid in small quantities, and also as a safety valve. Heat should not be applied until the oxide is thoroughly wetted by the acid. The gas may be washed by passing it through a small quantity of water in B. It is dried by passing it through strong sulphuric acid in C.

If the dry gas is wanted, it is collected by downward displacement, as represented in Fig. 37. The color of the gas easily shows when the jar is filled. The gas may then be kept for some time in the jar, if the stoppers are greased.

122. The gas can not be collected over cold water, because water at 10° C. absorbs 2.58 times its volume of chlorine. It may, however, be collected over warm water or brine.

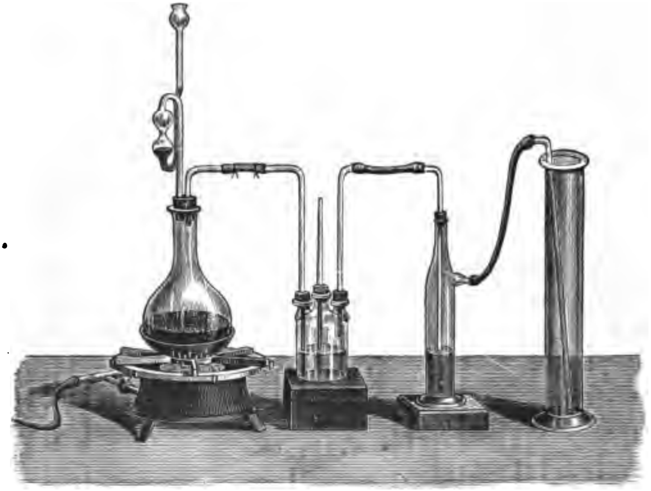


FIG. 37.

Exp. 85.—To prepare a solution of chlorine, or chlorine water, fill a retort with distilled water and place it in the position shown in Fig. 38. Carry a long delivery tube into the body of the retort, so that the chlorine may bubble through the water. Shake the retort from time to time, and keep it cool by pouring water on the outside. The operation may be stopped when the bubbles of gas are no longer absorbed.

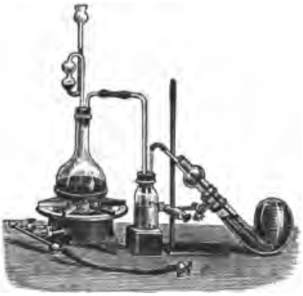


FIG. 38.

Chlorine water may be preserved for future use by storing it in bottles covered with black paper and kept in a cool place. It possesses most of the properties of the gas.

123. Physical properties. Chlorine is a greenish yellow gas of pungent odor. It is one of the heaviest gases, being 2.47 times heavier than air. It may be condensed at 12.5° C. to a yellow liquid (sp. gr. 1.33), by a pressure of 8.5 atmospheres; but it has never been solidified, even at—90° C.

FIG, 39.

Exp. 86.—To show its rapid absorption by water, hold a jar of chlorine gas downward in water, and decant one-third of it. Now close the mouth of the bottle with the hand, and shake the bottle. The water will completely absorb the gas, producing a vacuum in the bottle, which will then be held to the hand by atmospheric pressure.

When saturated chlorine water is cooled to 0° C., yellow crystals of $Cl, 5H_2O$, chlorine hydrate, may be obtained. These crystals are used as a source for obtaining liquid chlorine.

124. The chemical properties of chlorine are very active, and give rise to the various phenomena of combination, displacement and substitution, and indirect oxidation.

125. (I) **Combination.** Very nearly all the elements unite directly with chlorine.

Exp. 87.—Prepare several jars of the dry gas. Powdered antimony sprinkled into the chlorine forms $SbCl_5$, generally evolving flashes of light. A similar result follows by using powdered metallic arsenic or bismuth.

Exp. 88.—Place in a deflagrating spoon a piece of dry phosphorus, and plunge this into a jar of the gas. The two elements combine with a pale flame to form PCl_3 or PCl_5. (See Fig. 29.)

Exp. 89.—Stir gold leaf in chlorine water. It soon dissolves to $AuCl_3$.

126. (II) **Displacement and substitution.** The most important applications of chlorine depend on its affinity for hydrogen.

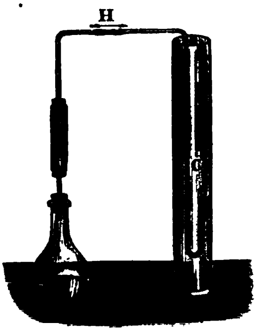


FIG. 40.

If a jet of burning hydrogen be introduced into a jar of chlorine, it will continue to burn with the formation of HCl. A mixture of the two gases combines slowly in diffused light, but suddenly and with explosive force in the direct sunlight. (See Exp. 56).

Exp. 90.—Pour chlorine water into a solution of hydrogen sulphide. The latter is decomposed with precipitation of sulphur, and hydrochloric acid is formed. $H_2S + 2\,Cl = 2\,HCl + \underset{\downarrow}{S}$.

Exp. 91.—To a tube two-thirds full of chlorine water add enough ammonia solution to fill it; then invert the tube in a capsule of water. Bubbles of nitrogen will rise to the top, and hydrochloric acid will be formed: $NH_3 + 3\,Cl = 3\,HCl + \overset{\uparrow}{N}$. The hydrochloric acid will then combine with another portion of the ammonia to form NH_3HCl, ammonium chloride.*

Exp. 92.—Wet strips of filter paper with *warm* turpentine, and plunge into a jar of dry chlorine. The turpentine will be decomposed; its hydrogen will unite with chlorine, and dense fumes of carbon will be evolved, as carbon does not unite directly with chlorine. (Fig. 41).

Hence, if lighted tapers be plunged into chlorine gas, they burn feebly with a smoky flame, only the hydrogen of the taper combining with the chlorine. (Fig. 42).

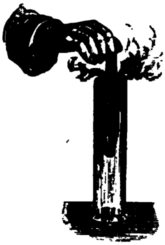


FIG. 41.

FIG. 42.

So, also, chlorine will decompose water. If a tube filled with chlorine water be inverted in water and placed in the sunlight, bubbles of oxygen will collect at the top of the tube. The hydrochloric acid formed dissolves in the excess of water. (See Exps. 7 and 28): $H_2O + 2\,Cl = 2\,HCl + \hat{O}$.

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* Care must be taken to keep the ammonia in excess; otherwise, a very explosive compound, nitrogen chloride ($NHCl_2$, NCl_3), will also be formed.

127. (III) **Indirect oxidation.** The last experiment shows that chlorine may be used as an oxidizing agent. When so used, the oxygen liberated is applied in the nascent state and is very energetic.

Exp 93.—Add to a solution of manganous sulphate a little potassium hydrate: white manganous oxide precipitates. Now add a few drops of chlorine water: black dioxide of manganese immediately forms; $MnO, H_2O + 2\,Cl = MnO_2 + 2\,HCl$,

128. Uses. (I) *Bleaching properties.* Dye stuffs are frequently organic compounds containing hydrogen. If chlorine acts upon such dyes in the presence of water, they are changed to colorless compounds as the result of chlorination or of oxidation. Hence, chlorine is an excellent bleaching agent.

Exp. 94.—Place strips of printed calico in chlorine water, or expose them in a damp state to the action of the gas. Most of the colors will soon disappear. Indigo first oxidizes to isatin, and then changes to chlorisatin, both of which are soluble in water and are nearly colorless.*

The experiment may be repeated with green leaves or flowers. Most mineral colors remain unaltered. Printers' ink is not affected at all, as it is largely carbon.

(II) *Disinfecting properties.* Among the noxious products of the decay of animal and vegetable matters are ammonia, hydrogen sulphide, and similar compounds. Chlorine acts upon these compounds in the same way that it acts upon coloring matters, and converts them into harmless substances. Hence it is of great value as a disinfectant.

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* C_8H_5NO (indigo) $+ H_2O + Cl_2 = C_8H_5NO_2$ (isatin) $+ 2\,HCl$.
$C_8H_5NO_2$ (isatin) $+ Cl_2 = C_8H_4ClNO_2$ (chlorisatin) $+ HCl$.

Tests.—Free chlorine may be recognized, (1) by its odor, (2) by its bleaching properties, and (3) by its producing a blue color in acting upon a mixture of starch and potassium iodide (Exp. 28).

129. Hydrochloric acid, HCl. Discovered by Priestley.

Preparation. — Introduce about 20 grammes of fused sodium chloride into a flask, and pour over it 40 grammes of sulphuric acid. Heat the flask very gently, and collect the gas by displacement in dry jars.*

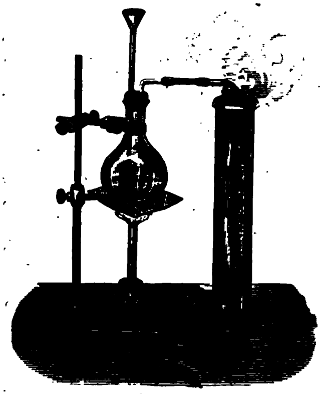

Fig. 43.

130. Physical properties. Hydrochloric acid is a colorless gas, having an acid taste and pungent odor. It has a specific gravity of 1.27, and may be condensed by a pressure of 40 atmospheres to a colorless liquid. At 15° C., one volume of water absorbs 400 times its volume of the gas.

Exp. 95.—Its solubility in water may be shown by fitting to a bottle containing the gas a cork furnished with a glass tube, and inverting the bottle over water. In a short time the water will rush into the bottle as if into a vacuum.

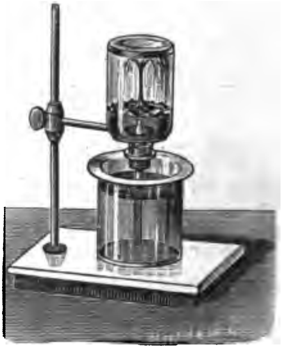

Fig. 44.

The commercial acid, frequently called muriatic acid, is made by passing the gas into a series of bottles containing cold water. (Fig. 45). When this acid has a specific gravity of 1.21, it contains 43 per cent, by weight, of HCl, and may be represented by the formula, $HCl + 3H_2O$.

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* $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$.

131. Chemical properties. Hydrochloric acid dissolves many metals and their oxides, forming with them chlorides which are represented by KCl, $FeCl_2$, and Fe_2Cl_6. All of the metallic chlorides are soluble in water except $AgCl$, Hg_2Cl_2, $PbCl_2$, $TlCl$, and Cu_2Cl_2. When hydrochloric acid acts upon an oxide, two atoms of chlorine are required to displace one atom of oxygen. Thus:

$$FeO + 2HCl = FeCl_2 + H_2O.$$
$$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O.$$

When no chloride so corresponding to the oxide exists, part of the chlorine is set free and a lower chloride formed. This is generally the case with the peroxides; as, MnO_2, PbO_2; $PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$.

TESTS.—HCl gas forms, with the vapor of ammonia, white fumes of NH_3, HCl. Solutions of HCl, or of the metallic chlorides, yield, with silver nitrate, a white, curdy precipitate, $AgCl$, soluble in ammonia, but insoluble in nitric acid.

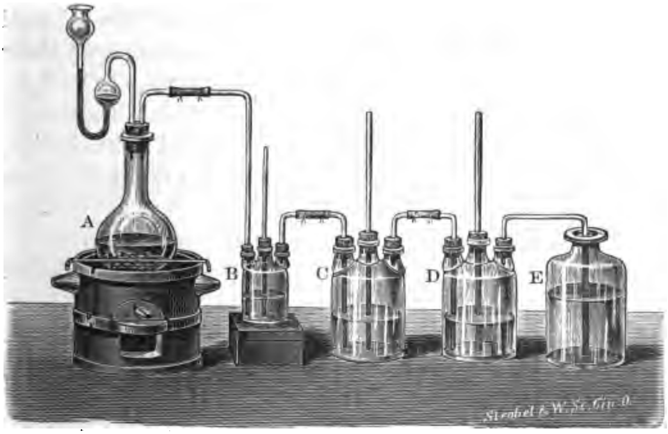

FIG. 45.

132. Uses. Enormous quantities of hydrochloric acid are evolved in the manufacture of soda. This acid is used as a source of chlorine in the manufacture of calcium hypochlorite. In the laboratory it finds constant employment as a convenient solvent.

133. The compounds of chlorine and oxygen. Chlorine forms the following series of acids, which may be regarded as formed from an anhydride, with the addition of one molecule of water, or as oxides of hydrochloric acid.

WATER.	ANHYDRIDE.	NAME OF ACID.	HCl.
H_2O, +	Cl_2O =	hypochlorous acid,	2 × $HClO$.
H_2O, +	Cl_2O_3 =	chlorous acid,	2 × $HClO_2$.
H_2O, +	Cl_2O_5 =	chloric acid,	2 × $HClO_3$.
H_2O, +	Cl_2O_7 =	perchloric acid,	2 × $HClO_4$.

Only the first two anhydrides have been isolated. The acids are seldom prepared. They are very unstable, and are liable to produce dangerously explosive compounds. Besides these, there exists chloric peroxide, Cl_2O_4, for which no corresponding acid is known.

134. Hypochlorites. The best known hypochlorites are sold under the names of "chloride of lime" and "chloride of soda." These are mixtures which owe their useful properties to the calcium hypochlorite, CaO, Cl_2O, and sodium hypochlorite, Na_2O, Cl_2O, which they contain. They are excellent bleaching and disinfecting agents. Hypochlorous acid is itself more energetic than chlorine, probably because, on breaking up, it evolves chlorine and oxygen, both in their nascent state.

We may study its properties by means of a solution prepared from good "chloride of lime."

Exp. 96.—Add to a little of the solution an equal amount of dilute sulphuric acid. Yellow fumes will be given off, which are hypochlorous acid.

Exp. 97.—Repeat the experiment, using only a few drops of the acid. Only chlorine will be liberated.

Exp. 98.—Place in each of the preceding mixtures, and also in a fresh quantity, paper which has been written upon, and notice the relative rapidity with which each is bleached.

Exp. 99.—Add a few drops of the solution to a solution of manganous chloride or of cobaltous nitrate; the black precipitates which fall are MnO_2 or Co_2O_3. The protoxides have acquired additional oxygen from the calcium hypochlorite.

Exp. 100.—Add a few drops of cobaltous nitrate to a pint of the solution, and heat. A large quantity of oxygen will be given off, which may be collected and tested. The cobaltic oxide seems to act as a carrier of the oxygen, first combining with it and then giving it off.

135. The hypochlorites are prepared by passing chlorine through or over the metallic hydrates.

Exp. 101.—Pass a slow current of chlorine gas into a cold dilute solution of potassium hydrate. The solution acquires strong bleaching properties from the formation of potassium hypochlorite.

$$K_2O, H_2O + 4\,Cl = K_2O, Cl_2O + 2\,KCl + H_2O.$$

136. The chlorates. If this solution be boiled, it will be converted into potassium chloride and potassium chlorate: $3(K_2O, Cl_2O_5) = 4\,KCl + K_2O, Cl_2O_5$ or $2(KClO_3)$.

Exp. 102.—Pass a rapid stream of chlorine gas into a moderately strong solution of potassium hydrate. The liquid will soon become hot enough to decompose the hypochlorite, and the ultimate result will be thus expressed:

$$6\,K_2O, H_2O + 12\,Cl = K_2O, Cl_2O_5 + 10\,KCl + 6\,H_2O.$$

If the solution be allowed to cool, tabular crystals of potassium chlorate will be deposited. If the solution be then poured off, and the crystals redissolved in boiling water, a second crop of crystals may be obtained, which are nearly pure potassium chlorate.

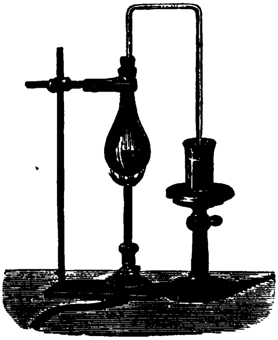

FIG. 46.

137. Chloric acid, H_2O, Cl_2O_5 or $HClO_3$. If a solution of potassium chlorate be mixed with hydro-fluo-silicic acid, potassium silico-fluoride is deposited, and hydrated chloric acid remains in the solution.

$$K_2O, Cl_2O_5 + 2HF, SiF_4 = 2KF, SiF_4 + H_2O, Cl_2O_5.$$

This solution concentrated *in vacuo* yields a syrupy, yellow liquid of peculiar odor. It inflames paper, sulphur, and phosphorus — sometimes with explosive violence. The acid and its salts are easily decomposed by heat and by the stronger acids, and are among the most energetic oxidizing agents known.

Exp. 103.—Powder *separately* equal weights of sugar and potassium chlorate, and then mix the powders carefully. The mixture, touched with a glass rod dipped in sulphuric acid, burns with a brilliant white light.

Exp. 104.—A little of the sugar mixture, wrapped in paper and struck by a hammer, detonates violently. If half of the sugar is replaced by dried potassium ferro-cyanide, it forms "white gunpowder."

Exp. 105.—Potassium chlorate forms with sulphur or phosphorus detonating compounds. If a *very little sulphur* be rubbed in a mortar with potassium chlorate, frequent explosions will take place.

138. Chloric peroxide and chlorous acid are dangerous to prepare on account of their explosive character.

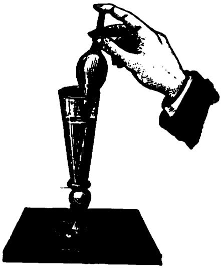

FIG. 47.

Exp. 106.—Drop a few crystals of potassium chlorate into a glass of water containing a few small slices of phosphorus. Now, by means of a pipette, add a little sulphuric acid to the bottom of the glass. A yellow gas, chloric peroxide (Cl_2O_4 or ClO_2), is formed, and oxidizes the phosphorus with bright flashes of light and slight detonations.

Exp. 107.—Add a few crystals of potassium chlorate to hydrochloric acid, and warm gently if no action immediately ensues. A yellow gas called *euchlorine* is evolved. It has very energetic bleaching and oxidizing properties, and is probably a mixture of chlorine with anhydrous chlorous and chloric acids.

139. Potassium perchlorate is formed when potassium chlorate is gently heated until the mass becomes pasty. One-third of the oxygen is given off, and the remainder is a mixture of potassium chloride and potassium perchlorate: $2(K_2O, Cl_2O_5) = K_2O, Cl_2O_7 + 2KCl + O_4$. If this mass is dissolved in hot water, and the solution allowed to cool, potassium perchlorate crystallizes out. Perchloric acid may be obtained from this salt by precipitating the potassium by hydro-fluo-silicic acid (§**137**).

The perchlorates do not yield Cl_2O_4 when treated with sulphuric acid. They have no commercial uses.

TESTS.—These experiments are also tests for the compounds of oxygen and chlorine. When heated, they are all converted to chlorides, and may then be tested as such.

BROMINE.

140. Bromine occurs in the waters of many saline springs and in sea water. When such liquids are evaporated, most of the other salts crystallize out, and the liquid remaining ("bittern") contains magnesium and sodium bromides.*

141. Preparation. These liquids are treated with chlorine, the bromine is set free, and the vapors which escape are collected in a cooled receiver. These consist of liquid bromine and an aqueous solution of bromine.

Exp. 108.—Add chlorine water to a solution of potassium bromide. Bromine will separate out and render the liquid yellowish red. Place this liquid in a separatory funnel (Fig. 48), and add a little ether. Shake the mixture and then allow it to stand. An ethereal solution of bromine will rise to the top.

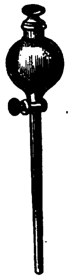

FIG. 48.

142. Physical properties. At 15° C., bromine is a dark red liquid of a disagreeable odor, from which it derives its name (βρῶμος, a stench): sp. gr. 2.96. It solidifies at —22°, boils at 63° C., and yields abundant vapors at ordinary temperatures. It is sparingly soluble in water; readily in ether and in carbonic disulphide.

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* Nearly 200,000 pounds of bromine are made in Ohio annually.

143. Its chemical properties are like those of chlorine. It has a strong affinity for hydrogen, and, therefore, may be used as an agent for indirect oxidation, for bleaching, and for disinfecting.

Exp. 109.—Vaporize a few drops of bromine in a jar, and introduce a pellet of dry phosphorus. PBr_3 is formed, with evolution of light.

With other jars test its bleaching properties, etc., as with Cl.

TESTS.—Free bromine is recognized by its odor, and by the orange color it gives to a starch solution.

The bromides give, with silver nitrate, yellowish white silver bromide, AgBr, which is converted by chlorine water into AgCl and free Br. The Br may be separated by shaking with ether.

144. Uses. The bromides are used in photography and in medicine. Free bromine is used in some chemical operations in preference to chlorine.

Bromine forms HBr (hydrobromic acid), H_2O, Br_2O (hypobromous acid), and H_2O, Br_2O_5 (bromic acid), which resemble the corresponding chlorine compounds.

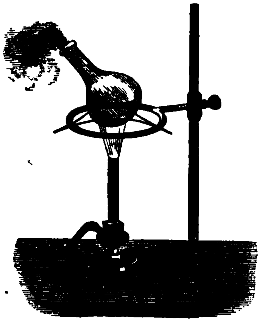
IODINE.

145. Iodine is contained in sea water in exceedingly minute quantities. Certain marine plants and animals contain it in such proportions that it can be obtained from their ashes with profit.

146. Preparation. The ashes of sea weed, called *kelp*, are treated with a little hot water, and the solution which forms is set aside to crystallize. The mother liquors contain sodium iodide, NaI. These liquors, heated with manganese dioxide and sulphuric acid, evolve free iodine, which is collected in cooled receivers. The iodine may also be isolated by chlorine. (Exps. 19 and 28).

147. Physical properties. Iodine is a grayish black, crystalline solid. It volatilizes at ordinary temperatures, melts at 115° C., and boils at 200° C., evolving the beautiful vapors from which it derives its name (*ἰώδης*, violet-colored).

It dissolves in 7,000 parts of water; readily in aqueous solutions of metallic iodides, in alcohol, ether, and chloroform. Its best solvent is carbonic disulphide.



FIG, 49.

Exp. 110. — (1) Volatilize a grain of iodine in a dry flask: (2) after the sublimate has cooled, dissolve it in a few drops of alcohol: (3) add water, and most of the iodine will precipitate: (4) shake a little of the aqueous solution in a test tube with ten drops of carbonic disulphide. On standing, the disulphide will settle to the bottom of the tube, and its color change to violet, owing to the dissolved iodine.

148. The chemical properties of iodine are less energetic than those of chlorine and bromine. Either of these elements displaces it from its haloid salts. Its bleaching powers are very feeble. We have already seen that it unites directly with other elements. (Exps. 10, 11, 12, 15). It acts corrosively upon organic tissues, staining the skin yellow.

TESTS.—Free iodine forms a beautiful blue color with starch paste, and a violet solution with CS_2.

The iodides give, with silver nitrate, a buff-colored AgI; with mercuric chloride, scarlet HgI_2. Any iodide treated with chlorine yields free iodine, which may then be tested with starch paste. An excess of chlorine should be avoided.

The iodine may also be set free by potassium nitrite acidulated with acetic acid.

149. Uses. Iodine is largely used in the manufacture of aniline green and in photography. The element and its salts are employed in medicine, especially for the treatment of enlarged glands.

150. Hydriodic acid, HI. Free hydrogen and iodine do not readily unite; but, when iodine is present with nascent hydrogen, the two elements unite to form hydriodic acid.

This is illustrated by Exp. 31. Nevertheless, hydriodic acid is a very unstable body. It is readily decomposed by the oxygen of the air, forming water and depositing iodine. It may even act as a reducing agent. In the experiment just cited, it is necessary that the solution of sulphurous acid be very dilute, for, otherwise, considerable sulphuric acid is formed, and is again reduced by the hydriodic acid to sulphurous acid.

$$H_2SO_4 + 2HI = H_2SO_3 + H_2O + 2I.$$

A solution of hydriodic acid is conveniently prepared by passing hydrogen sulphide through water containing iodine in suspension: $H_2S + 2I = S + 2HI$. The separated sulphur is filtered off, and the solution warmed to expel the excess of hydrogen sulphide.

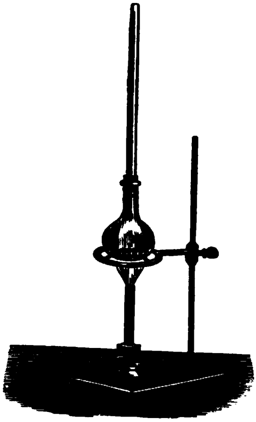


FIG. 50.

151. Oxides of iodine. Iodine has a much stronger affinity for oxygen than either chlorine or bromine. Iodic acid, H_2O, I_2O_5, may be obtained by heating iodine with strong nitric acid in a flask, to which is fitted a long glass tube that serves to condense the iodine which volatilizes unchanged. By heating this to 170° C., iodic anhydride,

I_2O_5, may be obtained. At about 370° it is decomposed. The acid forms iodates which closely resemble their corresponding chlorates.

There exist, also, periodic acid, H_2O, I_2O_7, and other compounds whose composition has not been determined with certainty.

Recapitulation.

The halogens are volatile elements which usually act as electro-negative monads.

Fluorine is characterized by a wonderful affinity for silicon.

Cl, Br, and I form a natural group whose relations to each other are more intimate than are those of any one of them to F.

All combine readily with hydrogen, forming acids which are soluble in water.

By reason of this affinity for hydrogen, Cl and Br act in the presence of H_2O indirectly as oxidizing, bleaching, and disinfecting agents.

All combine directly with most metals to form haloid salts. The most common in nature are those containing Na, K, Ca, or Al.

The haloid salts are frequently associated together in nature, and are generally isomorphous.

They tend to form double salts, as $2KI, HgI_2$. This is especially characteristic of the salts of fluorine, as $2KF, SiF_4$.

Fluorine forms no compounds with oxygen.

The oxy-salts of the others are easily decomposed, yielding the haloid salt and free oxygen. Hence, the oxy-salts may be used, either alone or with strong acids, as oxidizing agents.

CHAPTER VI.

THE SULPHUR GROUP.

ELEMENT.	SYMBOL.	SPECIFIC GRAVITY.		ATOMIC WEIGHT.	FUSING POINT.	DISCOVERER.
		SOLID. $H_2O = 1$.	VAPORS. AIR = 1.			
Sulphur	S	2.05	2.21	32.	120°	
Selenium	Se	4.79	5.48	79.5	250°	Berzelius, 1817.
Tellurium	Te	6.65	8.91	129.	500°	Klaproth, 1798.
Oxygen	O		1.106	16.		Priestley, 1774.

152. A natural gradation of properties is also exhibited by this group. Their specific gravities, melting points, and atomic weights form an increasing series. Their chemical energies are in a reverse order, sulphur being the most active and tellurium the least.

They are each characterized by forming fetid aëriform compounds containing two volumes of hydrogen to one of the other element—the three volumes condensing to two; as, H_2S, H_2Se. In this respect, oxygen is allied to this group, as also in the fact that each of them is capable of replacing oxygen in most of its compounds, atom for atom. Hence, they are generally ranked among the dyad elements; but they also form compounds in which they are quadrivalent, as SCl_4, and sexivalent, as $S(C_2H_4)''(C_2H_5)'_2 Br'_2$. Their highest atomicity, therefore, classes them as negative hexads.

153. Each element of this group forms two acid anhydrides with oxygen, and at least two acids, which have similar formulæ and properties.

Type, H_2O	Type, $2H_2O$ or $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\rangle O_2$			
	ANHYDRIDES	"OUS" ACIDS	ANHYDRIDES	"IC" ACIDS
H_2S	SO_2	H_2O, SO_2 or H_2SO_3	SO_3	H_2O, SO_3 or H_2SO_4
H_2Se	SeO_2	H_2O, SeO_2 or H_2SeO_3	SeO_3*	H_2O, SeO_3 or H_2SeO_4
H_2Te	TeO_2	H_2O, TeO_2 or H_2TeO_3	TeO_3	H_2O, TeO_3 or H_2TeO_4

The hydrogen of each of these compounds is replaceable by two atoms of a monad metal or by one atom of a dyad, to form corresponding salts; as, K_2S, K_2SO_4, CaS, $CaSO_4$.

154. The physical properties of tellurium ally this group to the metals. It conducts heat and electricity, though not readily, and has a brilliant metallic luster. Sulphur is a non-conductor of heat and of electricity, and has a vitreous luster. Selenium, a red solid, is midway between them. Finally, all three occur native,—selenium frequently associated with sulphur, tellurium associated with gold and other metals.

NOTE.—Lately an ore of gold has been found in Colorado combined with considerable quantities of tellurium; but tellurium and selenium are still so rare as to need no further description.

SULPHUR.

155. Sulphur is found native in considerable quantities. It occurs in many minerals as sulphides—*e. g.*, iron pyrites (FeS_2), copper pyrites (Cu_2S, FeS_2), galena (PbS), blende (ZnS), cinnabar (HgS); and as sulphates—*e. g.*, gypsum ($CaSO_4$), heavy spar ($BaSO_4$), Epsom salts ($MgSO_4$), and Glauber's salts (Na_2SO_4). It is also a constituent of many organic products, as casein, fibrin, albumin, and the oils of cruciferous and alliaceous plants, as mustard and garlic.

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* Selenic anhydride has not been isolated.

156. Preparation. In order to free it from its earthy impurities, native sulphur generally requires to be distilled.

The vapors are conducted into large brick chambers, and are there condensed. The flowers of sulphur are the first product obtained while the walls of the chamber are yet cold. After a time, the walls of the chamber become heated; the sulphur melts and is cast into wooden moulds to form roll sulphur or brimstone.

157. Physical properties. Sulphur is a brittle, yellow solid, tasteless and almost inodorous. On being heated, it becomes a limpid fluid at 120° C.: as the temperature rises, it darkens and thickens, until, at about 250° C., it is so viscid that the vessel in which it is contained may be inverted without spilling it: above 300° C. it again liquefies, boils at 440° C., and is converted into an orange vapor, which, at 500° C., has a density of 96, and at 1000° C., the normal density of 32.

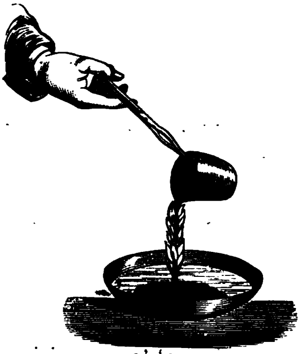


FIG. 51.

If, now, the vessel is removed from the flame, and a small quantity is poured into cold water, it forms an amorphous, elastic mass called *plastic sulphur*. The portion remaining in the vessel passes, as it cools, through the viscid and limpid states, and finally crystallizes in oblique prisms. If the liquid portion be poured off as soon as a crust has formed on the surface, the crystals will be found lining the interior walls.

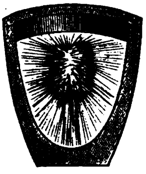


FIG. 52.

If, now, some of the crystals are dissolved in carbonic disulphide, and the solution is allowed to evaporate spontaneously, beautiful octahedral crystals are deposited, resembling those of native sulphur.

Plastic sulphur is not soluble in carbonic disulphide.

158. Sulphur has, then, at least three allotropic states: (1) the octahedral, (2) the oblique prismatic, and (3) the plastic. The milk of sulphur is another modification, obtained by precipitating sulphur from the alkaline polysulphides by the addition of acids. All of these are changed to the prismatic form by fusion, and all, on standing, assume more or less perfectly the octahedral condition.

Exp. 111.—Confirm these facts by performing the operations indicated. A test tube will suffice to show the changes assumed by heating; but, to obtain fine oblique prisms, a good-sized crucible is required.

159. Chemical properties. Sulphur enters into direct combination with many of the elements.

Exp. 112.—Heat in a test tube a mixture of sulphur with twice its weight of copper filings. The two elements unite with vivid combustion at a temperature a little above the melting point of sulphur. (See also Exp. 14).

The compounds with the metals are sulphides. These have, in general, properties and formulæ analogous to their corresponding oxides, as FeS, CuS.

Carbonic disulphide, CS_2, is formed by passing the vapor of sulphur over ignited coals. (See § 805).

Sulphur heated in the air inflames at 250° C., and burns with a pale blue flame, being converted into sulphurous anhydride, SO_2, and evolving peculiar, suffocating fumes, the same as are noticed in burning matches coated with sulphur.

160. Tests. Free sulphur is recognized by its physical properties and by its peculiar odor when burned.

Sulphur in combination may be detected by (1) placing in a small tube of very thin glass a little magnesium or sodium: (2) covering the metal with the substance to be tested, which must be perfectly free from water; and (3) then heating the mixture in the flame of a lamp. A vivid combustion ensues, and a sulphide (hepar) is formed. (4) On bringing this sulphide upon a bright silver coin, and moistening the mass with water, a black stain (Ag_2S) will be produced on the silver if sulphur is present.

The hepar may also be made by fusing a substance which contains sulphur upon coal, with sodium carbonate, before a flame free from sulphur.

161. Uses. Large quantities of sulphur are used in preparing its numerous compounds, as sulphuric acid, etc., in vulcanizing India rubber, and in making matches and gunpowder.

162. Hydrogen sulphide, also called sulphuretted hydrogen and hydrosulphuric acid, H_2S, occurs native in "sulphur springs," and is one of the causes of the odors of putrefying organic substances, as of rotten eggs.

163. Preparation. Hydrogen sulphide is generally prepared by decomposing ferrous sulphide with dilute sulphuric acid: $FeS + H_2O, SO_3 = FeO, SO_3 + H_2S$.

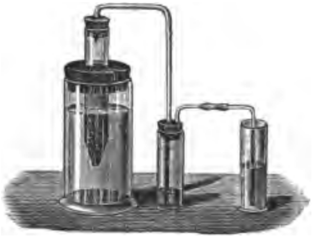


FIG. 53.

The process is similar to that described in Exp. 23. Fig. 53 exhibits an apparatus which is convenient when small quantities of the gas are wanted from time to time. A bit of glass tubing, made funnel-shaped at one end, contains the ferrous sulphide. It is supported by a cleft cork in the large cylinder, which contains the dilute acid. When the tube is pushed down into the cylinder, the acid enters through the mouth of the funnel, and the reaction begins. It may be stopped by lifting the tube out of the acid. The smaller cylinder contains a little water, in order to wash the gas.

164. Physical properties. Hydrogen sulphide is a colorless, coercible gas of extremely offensive odor: sp. gr. 1.178. At ordinary temperatures, water absorbs about three times its volume of the gas.

165. Chemical properties. The gas is readily inflammable, and burns with a blue flame like that of sulphur. Its solution is readily decomposed by chlorine, bromine, or iodine, by many oxidizing agents, and even by prolonged contact with the air. In such cases the sulphur is generally deposited, and the hydrogen unites with the chlorine, oxygen, etc. Hence, it may act as a reducing agent.

Exp. 113.—Add a few drops of calcium hypochlorite to a solution of hydrogen sulphide. The "milk of sulphur" is deposited.

$$CaCl_2O_2 + 2H_2S = CaCl_2 + 2H_2O + \underset{\downarrow}{S_2}.$$

Exp. 114.—Acidulate a solution of potassium bichromate with sulphuric acid, and then add hydrogen sulphide. On warming the solution a green color appears, which indicates the production of chromic sesquioxide:

$$K_2O, 2CrO_3 + 4H_2O, SO_3 + 3H_2S = K_2O, SO_3 + Cr_2O_3, 3SO_3 + 7H_2O + 3\underset{\downarrow}{S}.$$

Chromic anhydride is reduced to chromic sesquioxide, and ferric salts to ferrous salts:

$$2CrO_3 + 3H_2S = Cr_2O_3 + 3H_2O + \underset{\downarrow}{S_3};$$
$$Fe_2Cl_6 + 2H_2S = 2FeCl_2 + 2HCl + \underset{\downarrow}{S_2}.$$

166. Uses. Besides this reducing action, it is largely employed in the laboratory as a group reagent.

I. It precipitates from their solutions Hg, Pb, Ag, Cu, Cd, Bi, as sulphides, insoluble in dilute acids or in alkaline sulphides.

II. It precipitates from solutions feebly acid As, Sb, Sn, Au, Pt, as sulphides, which act as sulpho-acids, and combine with the alkaline sulphides to form sulpho-salts that are soluble in water. Hence, these elements are not precipitated in alkaline solutions.

III. The sulphides of Ni, Co, Fe, Mn, Zn, U, are soluble in dilute acids; hence, they are precipitated only in alkaline solutions or by alkaline sulphides.

IV. Aluminium and chromium do not form sulphides in the wet way, but are precipitated as oxides by the alkalies in presence of hydrogen sulphide.

V. The sulphides of the more electro-positive elements, as Mg, K, are easily soluble in water, and, hence, are not precipitated by H_2S.

Exp. 115.—Arrange five test glasses to represent these groups. Pour a solution of arsenious acid into I, of lead nitrate into II, ferric chloride into III, alum into IV, potassium hydrate into V, and pass a current of the gas into each of these. Yellow AsS_3 will form in I; black PbS, in II; white S, in III, from a reduction of Fe_2Cl_6 to $FeCl_2$; and no apparent reaction will take place in the others. Now add a little of V to the AsS_3—it redissolves; to the PbS—it is unchanged; to a fresh solution of ferric chloride—black FeS precipitates; to alum—white $Al_2O_3, 3\,H_2O$ falls. Add ammonia to III and IV: the same change occurs as in the last two examples.

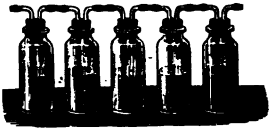


Fig. 54.

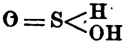
Tests.—Hydrogen sulphide may be recognized by its odor and by its reactions upon members of group I. Strips of "lead paper," made by dipping unsized paper into a solution of lead acetate, are very useful for this purpose. The alkaline sulphides strike a purple color with sodium nitro-ferro-cyanide, even in very dilute solutions.

167. Physiological properties. The gas is exceedingly poisonous when breathed, and, even when much diluted, it gives rise to nausea and vertigo.

168. The compounds of sulphur and oxygen. Two anhydrides of sulphur have been isolated—sulphurous anhydride, SO_2, and sulphuric anhydride, SO_3. They each combine with one molecule of water to form sulphurous acid, H_2O, SO_2, and sulphuric acid, H_2O, SO_3. These are of great use in the arts. There exists, also, a series of acid compounds containing more than one atom of sulphur, which are known collectively as the polythionic series (*θειον*, sulphur). Of this series, only the thiosulphates are of commercial importance.

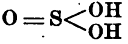
The acid compounds may be arranged as follows. Several formulæ are given of each, to illustrate different methods of notation.

I. MONOTHIONIC SERIES.



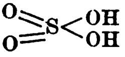
$O=S<^{H}_{OH}$ or $H'(SO)''(OH)'$ or $H_2O, SO(?)$ or H_2SO_2.

Hydrosulphurous or hyposulphurous acid.*



$O=S<^{OH}_{OH}$ or $(SO)''(OH)'_2$ or H_2O, SO_2 or H_2SO_3.

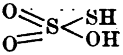
Sulphurous acid.



$\begin{matrix} O \\ O \end{matrix} \gtreqqless S<^{OH}_{OH}$ or $(SO_2)''(OH)'_2$ or H_2O, SO_3 or H_2SO_4

Sulphuric acid.

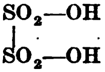
II. POLYTHIONIC SERIES.



$\begin{matrix} O \\ O \end{matrix} \gtreqqless S<^{SH}_{OH}$ or $(HS)'(SO_2)''(OH)'$ or H_2O, S_2O_2 or $H_2S_2O_3$.

Hyposulphurous or thiosulphuric acid.*

III.

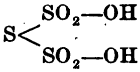


$\begin{array}{l} SO_2{-}OH \\ | \\ SO_2{-}OH \end{array}$

or

$H_2S_2O_6$

Dithionic acid.

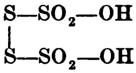


$S<\begin{array}{l} SO_2{-}OH \\ SO_2{-}OH \end{array}$

or

$H_2S_3O_6$

Trithionic acid.

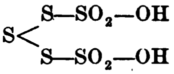


$\begin{array}{l} S{-}SO_2{-}OH \\ | \\ S{-}SO_2{-}OH \end{array}$

or

$H_2S_4O_6$

Tetrathionic acid.



$S<\begin{array}{l} S{-}SO_2{-}OH \\ S{-}SO_2{-}OH \end{array}$

or

$H_2S_5O_6$

Pentathionic acid.

169. **All these acids are dibasic**; that is, their hydrogen may be exchanged for one dyad or for two monad atoms. If both hydrogen atoms are thus replaced, the salt is normal, as K_2SO_4, potassium sulphate; if only one hydrogen atom is replaced by a monad, the salt is acid, as $KHSO_4$, acid potassium sulphate, or bisulphate of potassa. If two different metals take the place of the hydrogen, the resulting salt is double, as $K'_2Cu''(SO_4)_2 + 6H_2O$.

170. **Sulphurous anhydride,** SO_2, is found in nature among the gases issuing from volcanoes. No considera-

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* A lamentable confusion exists in the names of the first and fourth. By strict analogy, salts of the first should be called hyposulphites, as Na_2SO_2; but long use has given salts of the fourth acid; as $Na_2S_2O_3$, the name hyposulphites, and it is difficult to change a name which has become familiar. They should be called thiosulphates.

ble quantity is found in the air of towns, although it must be continually evolved in the burning of coals which contain sulphur.

171. Preparation. Sulphurous anhydride is the sole product of the combustion of sulphur in oxygen. It is generally prepared for laboratory purposes by heating strong sulphuric acid with either mercury or copper.

$$2(H_2O, SO_3) + Cu = CuO, SO_3 + 2H_2O + SO_2.$$

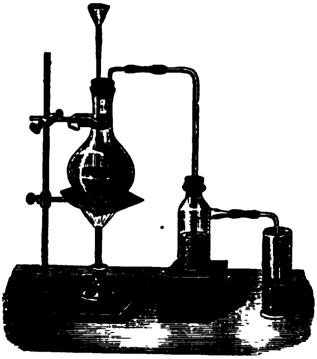

Fig. 55.

Exp. 116.—Heat in a flask 20 grammes of copper clippings with 60 cc. (Fig. 35) of strong sulphuric acid. Collect a portion of the gas by displacement in dry cylinders, and then form a solution of the gas by passing it into water. (Fig. 55). When the operation is finished and the flask is cooled, there will be found a grayish powder at the bottom of a brown liquid. Decant the liquid, add a little water to the powder, boil, and filter. After a little while, crystals of blue cupric sulphate will be formed in the filtrate. Often there remains on the filter a dark powder which is insoluble in water: this is a sulphide of copper, formed by the complete reduction of the sulphuric acid.

$$(a)\ H_2O, SO_3 + 4\,Cu = CuS + H_2O + 3\,CuO.$$
$$(b)\ 3\,CuO + 3\,(H_2O, SO_3) = 3\,(CuO, SO_3) + 3\,H_2O.$$

172. Physical properties. Sulphurous anhydride is a colorless, easily coercible gas of a pungent, suffocating odor: sp. gr. 2.25. It condenses, at —10° C., to a colorless fluid, which solidifies at —79° C.

Exp. 117.—Pass the gas from the flask in which it is generated, (1) into an empty bottle surrounded by ice, in order to cool it; then (2) through a chloride of calcium tube, to dry it; and (3) into a U tube surrounded by a mixture of ice and salt. (Fig. 56).

Sulphurous anhydride condenses, and may be preserved in sealed tubes or in soda water bottles.

FIG, 56.

Liquid sulphurous anhydride produces, by its evaporation, cold so intense as sometimes even to freeze itself. It freezes water readily,* and mercury if the evaporation is assisted by a brisk current of air. Water at 15° C. absorbs 45 times its volume of the gas, forming sulphurous acid, H_2O, SO_2. On freezing this solution, a crystallized hydrate is obtained, which is thought to have the formula $H_2SO_3, 14H_2O$.

173. Chemical properties. Sulphurous anhydride rapidly extinguishes the flame of ordinary combustibles. If a pan of burning sulphur is placed at the base of a chimney on fire, the flame of the burning soot is extinguished. Nevertheless, many metals in a finely divided state burn when heated in an atmosphere of this gas.

A solution of sulphurous acid exposed to the air slowly takes up oxygen and becomes sulphuric acid. This tendency to absorb oxygen renders the acid and its salts powerful reducing agents. (See Exp. 31).

Exp. 118.—Add a few drops of sulphurous acid to a weak solution of potassium permanganate. The red color disappears.

174. Sulphurous acid is an excellent bleaching agent for wool, silk, and straw. The bleaching is not always permanent, since the acid does not seem to decompose the coloring matters, but to form unstable, colorless compounds with them; as, in course of time, the color reappears.

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* See Norton's Philosophy, Art. 577.

Exp. 119.—Add a little sulphurous acid to a decoction of red cabbage previously rendered green by a drop of potassium hydrate: the color disappears. Now divide the liquid into two portions: to the first, add potassium hydrate—the green reappears; to the second, add sulphuric acid—the liquid becomes red.

Exp. 120.—Place in a bell glass a bunch of damp flowers over a crucible containing burning sulphur. (Fig. 57). Many of the flowers will be bleached. On dipping some of them afterward into sulphuric acid, and others into ammonia, their colors will be partly restored, but generally modified, by the action of the acid or of the alkali.

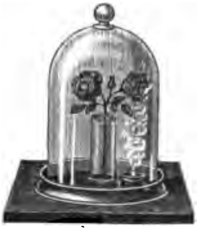
FIG. 57.

175. Sulphurous acid and its salts are valuable antiseptics; that is, they have the power of preventing or of arresting fermentation. For this reason cider barrels are "sulphured," in order to prevent the action of any substance capable of exciting fermentation in the new cider. For a similar reason calcium sulphite is frequently added to sweet cider. The air of rooms may be disinfected by burning sulphur in them.

TESTS.—Free sulphurous acid is readily recognized by its odor. The sulphites evolve SO_2 when treated with dilute sulphuric acid. If zinc be added to this mixture, the SO_2 is reduced to H_2S, which may be recognized by blackening lead paper.

176. Uses. Sulphurous acid is used for its bleaching and antiseptic properties. The acid sodium sulphite, NaH,SO_3, is used by paper makers as an *antichlore*, to prevent a destruction of the fiber through an excessive action of chlorine in bleaching.

177. Sulphuric anhydride, SO_3, may be formed by passing a mixture of dried sulphurous anhydride and oxygen through a tube containing heated platinum sponge. It is prepared more conveniently from the Nordhausen oil of vitriol. On gently heating this, the anhydride is disengaged, and may be collected in dry receivers cooled by ice.

178. Physical properties. Sulphuric anhydride crystallizes in white, feathery groups resembling asbestos. When perfectly dry it may be handled without inconvenience, and does not exhibit acid properties. Exposed to the air it absorbs water and becomes sulphuric acid. It is then very corrosive. Dropped into water it hisses like red-hot iron.

179. Chemical properties. The vapor of sulphuric anhydride passed over heated baryta or lime converts these bases into sulphates, with vivid incandescence.

180. Sulphuric acid, $H_2O, SO_3 = H_2SO_4$, has been found free in certain mineral waters, notably so in the Rio Vinagre of South America. It results, also, from the oxidation of sulphur and hydrogen sulphide.

181. Preparation. Sulphuric acid is prepared in enormous quantities by the oxidation of sulphurous anhydride in the presence of water.

Exp. 121.—Plunge into a jar of sulphurous anhydride a glass rod which has been dipped in fuming nitric acid. Red fumes appear, which show that the nitric acid has been reduced. In a little while the red color disappears, and a crystalline substance forms on the sides of the jar. Now, if a little water be shaken on the sides of the jar, the crystals dissolve with effervescence, the red fumes again appear, and the water contains sulphuric acid.

Exp. 122.—This process may be repeated on a larger scale by the apparatus shown in Fig. 58. A is a large globe fitted with a cork through which are passed five tubes, three of which are connected with the generating flasks, a, b, c.

I. The flask, b, contains copper filings. On pouring a very little nitric acid on these, nitric oxide is formed:

$$3\,Cu + 4\,(H_2O, N_2O_5) = 3\,(CuO, N_2O_5) + N_2O_2 + 3\,H_2O.$$

II. When this nitric oxide is mixed with the air of the flask and of the globe, it forms red fumes which are nitrogen peroxide:

$$N_2O_2 + \text{air or oxygen} = N_2O_4.$$

III. When the globe is filled with the nitrogen peroxide, evolve sulphurous anhydride from the flask, a, containing copper and strong sulphuric acid.

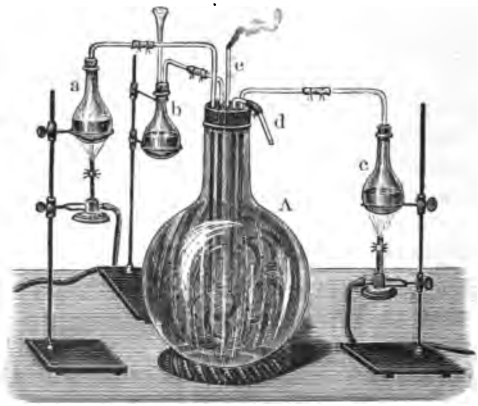

Fig. 58.

IV. The sulphurous anhydride will soon reduce the nitrogen peroxide to nitric oxide, the contents of the globe becoming colorless: $2SO_2 + N_2O_4 = 2SO_3 + N_2O_2$. The crystalline compound forms on the side of the flask. The structure of these crystals is unknown, but we may assume them to be $N_2O_2, 2SO_3$.

V. Now let steam be passed into the globe from the flask, c, which contains water. The crystals effervesce, and dilute sulphuric acid collects at the bottom of the globe.

$$N_2O_2, 2SO_3 + 2H_2O = 2(H_2O, SO_3) + N_2O_2.$$

The process is now finished. To render the process continuous, air must be blown from time to time through the tube, d, into the globe. The N_2O_2 liberated by the last reaction again becomes N_2O_4. Hence, but very little nitric oxide is necessary for the production of a large amount of sulphuric acid. It acts as a carrier of oxygen from the air to the sulphurous anhydride. The tube, e, allows the nitrogen of the air to escape.

It is scarcely necessary to mention, if these different steps occur simultaneously, that none of the crystalline compound will be deposited, as it is at once decomposed in the presence of water.

In sulphuric acid manufactories, the glass globe is replaced by a series of enormous leaden chambers. The sulphurous acid is generated by burning sulphur or iron pyrites in a furnace so arranged that the proper quantity of air may enter the chambers with the sulphurous anhydride. The nitric acid vapor is evolved from a mixture of sodium nitrate and sulphuric acid contained in an iron pan, which is heated by the combustion of the sulphur. Jets of steam are introduced at various parts of the chambers, and water is allowed to cover the floors. The sulphurous anhydride reduces the nitric acid, and combines with oxygen and water to form sulphuric acid. Provision is made to allow the nitrogen of the air, which takes no part in these changes, to escape, and, at the same time, to prevent loss by absorbing the nitrogen oxides for future use.

The acid is allowed to collect in the chambers until it has a specific gravity of 1.55. It is then drawn off and evaporated in leaden pans until it reaches the specific gravity of 1.72. Farther concentration is effected in platinum stills.

The commercial acid has a specific gravity of 1.82, and is known as oil of vitriol. This oil of vitriol frequently contains lead, arsenic, and other impurities.

182. Physical properties. Pure, concentrated sulphuric acid is an oily, colorless, inodorous liquid, having the specific gravity of 1.842. It boils at 327° C., and solidifies at —35° C. It is remarkable for its great attraction for water.

Exp. 123.—Place four ounces of water in a beaker, and pour into it a pint of strong sulphuric acid in a thin stream. The temperature often rises to 100° C. If the mixture be stirred with a thin test tube containing alcohol, the alcohol will boil.

When exposed to the air, sulphuric acid will often double its weight in a few days; hence it is often used as a dessicating agent.

Gases are dried by allowing them to pass over pumice stone soaked in strong sulphuric acid, or through a bottle containing the acid. Other bodies are dried by placing them in shallow vessels over a dish of sulphuric acid, and covering the whole by a bell glass so as to exclude the air. By conducting this operation *in vacuo*, water may be frozen by its own evaporation.

183. Chemical properties. Sulphuric acid also abstracts water from many organic substances, charring them or giving rise to new compounds.

Exp. 124.—Drop a lump of sugar into strong sulphuric acid: in a short time it will become carbonized.

Organic tissues moistened with the dilute acid are destroyed, from the gradual concentration of the acid by evaporation.

Strong sulphuric acid is reduced to sulphurous acid when heated with charcoal, sulphur, or the ordinary metals. The metals are thereby converted to oxides which form sulphates with another portion of the acid (Exp. 116). On the other hand, metals of the zinc and iron groups, except copper, when treated with the dilute acid, displace the hydrogen to form their sulphates (§ **81**). The sulphates are also formed when the acid is made to act upon metallic oxides, or upon their compounds with nearly all other acids. The acid is, therefore, one of the most energetic known.

TESTS.—Free sulphuric acid and solutions of its salts give, with barium chloride, a white, insoluble precipitate. Similar precipitates are given by strontium chloride and calcium chloride.

184. Uses. Sulphuric acid is used in the preparation of most other acids, in the manufacture of soda, phosphorus, and alum, and is employed, directly or indirectly, in nearly all important chemical processes. It is the most important chemical reagent we have. Over 100,000 tons are annually consumed in Great Britain alone.

185. Nordhausen oil of vitriol is obtained by heating dried ferric sulphate in earthen retorts. The acid which distills over is probably a compound of sulphuric anhydride and sulphuric acid: $SO_3H_2SO_4 = H_2S_2O_7$.

186. Properties. Nordhausen acid fumes in the air when the bottle containing it is opened. It is a little heavier than the ordinary acid, and is usually of a brownish color. Its salts are sometimes called *anhydrosulphates*, as $K_2S_2O_7$.

187. Uses. It is chiefly used for dissolving indigo in preparing the well-known Saxony blue dye.

188. Thiosulphuric acid, $H_2S_2O_3$, has not been isolated. Its salts are generally known as hyposulphites.

Sodium hyposulphite is prepared by boiling sodium sulphite with sulphur.

$$Na_2O, SO_2 + S = Na_2O, S_2O_2 \text{ or } Na_2S_2O_3.$$

It may be obtained in prismatic crystals, having the formula $Na_2S_2O_3, 5H_2O$.

Sodium hyposulphite is used for preparing other hyposulphites, and finds extensive employment in "fixing" photographic prints.

Exp. 125.—Prepare a little silver chloride by adding hydrochloric acid to silver nitrate, and wash with water by decantation. To one portion, suspended in water, add sodium hyposulphite. The silver chloride will change to silver hyposulphite, and dissolve: $2\,AgCl + Na_2S_2O_3 = 2\,NaCl + Ag_2S_2O_3$. Expose another portion to the sunlight; it darkens from the formation of a silver subchloride. On treating this with sodium hyposulphite, the silver subchloride is decomposed into silver chloride, which dissolves as before, and into metallic silver, which is left in a very finely divided state as a black powder. The photographer repeats this last process, except that he performs the operation upon paper which has been impregnated with silver chloride, and completes the process by washing out all the hyposulphite, so as to leave only the silver which has been reduced. (See § **398**).

Test.—The hyposulphites treated with hydrochloric acid evolve sulphurous anhydride, and deposit yellow sulphur.

189. Haloid compounds of sulphur. Sulphur forms compounds with chlorine, bromine, and iodine. One of these compounds—the disulphide of chlorine, Cl_2S_2—is employed as an agent in vulcanizing caoutchouc. It is a liquid formed by passing chlorine through the vapor of sulphur.

Comparison of Oxygen and Sulphur.

I. Oxygen and sulphur combine directly with most of the elements to form anhydrides.

Basic oxides; as, K_2O.	Basic sulphides; as, K_2S.
Indifferent oxides; as, MnO_2.	Indifferent sulphides; as, FeS_2.
Acid oxides; as, As_2O_3.	Acid sulphides; as, As_2S_3.

II. The anhydrides may unite together, forming—

Oxy-salts; as, K_2O, As_2O_3.	Sulpho-salts; as, K_2S, As_2S_3.

III. They may also combine with H_2O or with H_2S to form—

Hydrates; as, K_2O, H_2O.	Sulpho-hydrates; as, K_2S, H_2S.

Heat alone decomposes:

The oxides and sulphides of the noble metals; as, PtO_2, PtS_2.
Many of the higher oxides and sulphides; as, I_2O_5, I_2S_2.
And reduces some; as, MnO_2 to Mn_3O_4, and FeS_2 to FeS.

Hydrogen nascent, or passed over heated oxides and sulphides, reduces many of them.

$CuO + H_2 = Cu + H_2O.$ $Ag_2S + H_2 = Ag + H_2S.$

Heated carbon reduces the oxides and sulphides of most metals.

$Fe_2O_3 + 3\,C = Fe_2 + 3\,\overset{\frown}{C}O.$ $2\,FeS + C = 2\,Fe + C\overset{\frown}{S}_2.$

Chlorine may also decompose them, uniting with the more electro-positive element.

$H_2O + Cl_2 = 2\,HCl + \overset{\frown}{O}.$ $H_2S + Cl_2 = 2\,HCl + \underset{\smile}{S}.$

CHAPTER VII.

THE NITROGEN GROUP.

ELEMENT.	SYMBOL.	SPECIFIC GRAVITY.			ATOMIC WEIGHT.	FUSING POINT. °C.	DISCOVERER.
		SOLID.	AËRIFORM.				
		$H_2O = 1.$	AIR = 1.	H = 1.			
Nitrogen	N		0.969	14	14.		Rutherford, 1772.
Phosphorus	P	1.83	4.29	62	31.	44°	Brandt, 1669.
Vanadium	V	5.5			51.3		Sefström, 1830.
Arsenic	As	5.73	10.34	150	75.	180°	Schröder, 1694.
Antimony	Sb	6.7		244?	122	450°	Valentine, ? 1480.
Bismuth	Bi	9.9			210	264°	Agricola, 1529.
Niobium	Nb	6.27			94.		Hatchett, 1801.
Tantalum	Ta	10.78			182		Ekeberg, 1802.

190. The members of this group yield analogous compounds, as exhibited in the following schedule:

HYDRIDES, . . H_3N, H_3P, H_3As, H_3Sb.

CHLORIDES, . . NCl_3, PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$.

$$\text{ANHYDRIDES, }\begin{cases} N_2O_3, & P_2O_3, & As_2O_3, & Sb_2O_3, & Bi_2O_3. \\ N_2O_5, & P_2O_5, & As_2O_5, & Sb_2O_5, & Bi_2O_5. \end{cases}$$

191. The hydrides are fetid, inflammable gases, in which three atoms of hydrogen are united with one atom of the other element, and condensed to two volumes. No hydrides of vanadium or bismuth are known, but there exists a complete series of trichlorides. These compounds indicate that the elements of this group are triads; but they also play the part of pentads in a number of compounds, and hence are variously classed by chemists as triad and as pentad elements. All of these elements form at least two compounds with oxygen.

192. Vanadium is quite rare. It has chlorides which are both perissads and artiads, as VCl_2, VCl_3, and VCl_4,—which is an unexplained anomaly. Niobium, sometimes called columbium, and tantalum are still rarer elements.

NOTE.—All these agree in forming oxides of the formula R_2O_5, and other compounds which place them in this group. They are, however, not of sufficient importance to be considered further.

193. The other elements of the group manifest the gradational character noticed in the preceding groups. Nitrogen and phosphorus are, without doubt, non-metals: bismuth presents all the physical characters of the metals: arsenic and antimony may be considered as semi-metals, or as a connecting link between the non-metals and the metals. They have many of the physical properties of the metals and the chemical properties of the non-metals. Arsenic very closely resembles phosphorus in its oxygen compounds, and antimony in its sulphides and in its physical properties. Its atomic weight is also very nearly the mean between the two others. Similarly, antimony is allied on the one hand to phosphorus, and on the other to bismuth.

The sesquioxides of this group are acid anhydrides in nitrogen, phosphorus, and arsenic, feebly acid or feebly basic in antimony, and basic in bismuth. The highest oxides are all acid anhydrides, but the acid properties of bismuthic oxide are very feeble.

NITROGEN.

194. Nitrogen forms four-fifths of the volume of the air. The air also contains traces of ammonia, NH_3. It is found in most animal and in many vegetable substances. It also occurs in the form of sodium and potassium nitrates, and of the ammoniacal salts.

195. Preparation. Nitrogen may be obtained from the air by potassium pyrogallate (Exp. 78), or by burning in it any substance which forms with oxygen a product that may easily be removed.

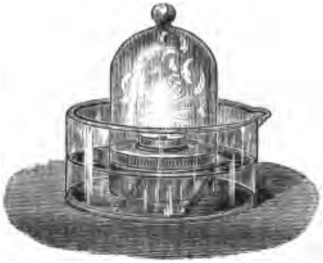

FIG. 59.

Exp. 126.—Place a dried slice of phosphorus in a capsule; float it on the surface of water, and ignite it. Now cover it with a bell glass. The oxygen within the bell will be consumed, and white clouds of phosphoric anhydride be formed. These will soon be absorbed by the water, and the gas remaining is nearly pure nitrogen. Nitrogen may also be obtained by boiling a solution of potassium nitrite mixed with thrice its volume of a strong solution of ammonium chloride: $NH_4Cl + KNO_2 = KCl + 2H_2O + 2\hat{N}$.

196. Physical properties. Nitrogen is a colorless, odorless, tasteless, permanent gas.

197. Chemical properties. Free nitrogen is remarkable for its chemical inactivity. It is neither combustible nor a supporter of combustion. At elevated temperatures it combines with titanium, carbon, oxygen, and a few other elements. It also unites with nascent hydrogen: thus, when iron rusts in moist air, a little ammonia is frequently found absorbed by the ferric oxide.

The organic compounds of nitrogen are exceedingly prone to decomposition. The mineral compounds are often unstable and explosive, as is especially the case with those that contain the radical nitryl (NO_2). This character of instability renders many of the nitrogen compounds energetic chemical agents.

Tests.—A gas which does not give any reaction with any known chemical test may be pronounced nitrogen. Solid organic matters containing nitrogen, when heated with a mixture of caustic soda and lime, yield ammonia H_3N.

198. Uses. The use of free nitrogen in the air appears to be to prevent the too rapid action that would take place in pure oxygen.

AMMONIA, H_3N.

199. Ammoniacal compounds are but sparingly found in nature, although ammonia is constantly produced in the putrefaction of animal and vegetable matters. The reason for this seems to be that plants derive their chief supply of nitrogen from the salts of ammonia, which are brought down by the rain from the atmosphere, and so consume it as rapidly as it is formed.

200. Preparation. The commercial source of ammonia and its compounds is the so-called sal-ammoniac , or ammonium chloride, NH_4Cl. This is obtained in large quantities in the process of making illuminating gas from coal.

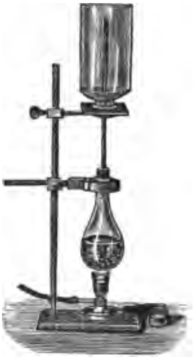

FIG. 60.

Exp. 127.—Rub together 30 grammes of pulverized sal ammoniac and 60 grammes of powdered quicklime. The heat caused by the friction will be sufficient to evolve the gas.

Exp. 128.—To collect the gas, pour this mixture into a flask to which a tube has been fitted; then add 60 cc. of water, and heat. Collect by upward displacement. (Fig. 60). It may be dried by passing it through a bottle containing lumps of quicklime.

$$2(NH_4Cl) + CaO = CaCl_2 + H_2O + 2H_3N.$$

Exp. 129.—It may also be collected for purposes of experiment by gently heating aqua ammonia and drying the gas.

201. Physical properties. Ammonia is a colorless, coercible gas of a pungent odor: sp. gr. 0.59. Aqua ammonia is a solution of the gas in water, obtained by passing a stream of the gas through bottles containing water, and kept cool by ice. One volume of water at 15° C. absorbs 783 volumes of the gas, and increases in volume one-half: sp. gr. 0.85. This solution is the aqua ammonia of commerce. The amount of the gas retained in the solution varies with the temperature and pressure.

Exp. 130.—Fill a barometer tube over 30 inches long with one inch of concentrated aqua ammonia and sufficient mercury to occupy the remaining space, and invert the tube under mercury. On removing the finger the Torricellian vacuum will be formed, and the ammonia solution will boil from the escape of a large quantity of the gas. (Fig. 61). The gas may be re-absorbed on depressing the tube in a tall cylinder of mercury, because of the increased pressure. It may then be re-expelled by pouring hot water on the top of the tube.

Exp. 131.—To show the rapid absorption of ammonia by water, Exp. 95 may be repeated with dry ammonia gas.

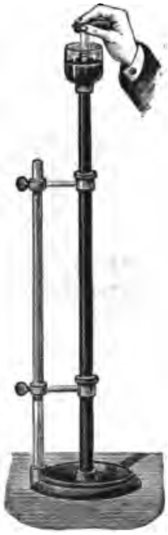

FIG. 61.

The gas may be condensed at —40° C. to a clear liquid which solidifies at —75° C. It may also be liquefied at 10° C. by a pressure of six atmospheres. The liquid evaporates rapidly and absorbs a large amount of heat. Carré's freezing apparatus utilizes these properties of ammonia in the production of artificial ice.

202. Chemical properties. The feeble combustible power of ammonia has already been shown in Exp. 49. Both the gas and the solution have strong alkaline properties, which will be considered in the chapter on alkalies.

Tests.—Free ammonia is detected (1) by its odor; (2) by its action on moistened red litmus paper; (3) by giving white fumes of NH_4Cl when a glass rod dipped in HCl is brought in contact with it.

Ammoniacal salts yield free NH_3 when heated with soda-lime or with KHO. *Traces* of aqua ammonia or of ammoniacal salts are detected by forming a brownish precipitate on the addition of "Nessler's test." *

203. Ammonia derivatives. Each of the hydrogen atoms in ammonia may be exchanged for a monad radical (elementary or compound), and thus give rise to new compounds which may be considered as formed on the type of one or more molecules of ammonia.

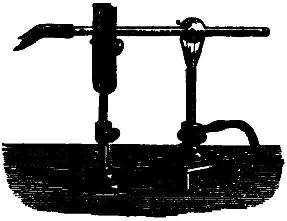

Fig. 62.

(I) When a positive radical takes the place of the hydrogen, an *amine* compound is formed. Thus, potassamine forms when dry ammonia gas is passed over a clean pellet of potassium, gently heated.

$$H_3N + K = KH_2N + H.$$

If potassamine is strongly heated, it becomes tripotassamine: $3KH_2N = K_3N + 2H_3N$.

(II) When a negative radical takes the place of the hydrogen, an *amide* compound is formed.

Exp. 132.—Rub together a gramme of iodine and 16 cc. of aqua ammonia. On standing for a few minutes, a brown powder, usually called iodide of nitrogen, is formed.

$$3H_3N + I_4 = I_2\underbrace{HN}_{} + 2(NH_4I).$$

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* This is prepared by adding to a gramme of KI, dissolved in H_2O, enough $HgCl_2$ to re-dissolve the precipitate which forms. Four grammes of KHO are then added, and water enough to make the volume of 100 cc. The liquid is then allowed to stand until it becomes clear, and the solution is preserved in tightly corked bottles.

$$4HgK_2I_4 + 6KHO + 2(NH_3H_2O) = \underbrace{Hg_4N_2I_2, 2H_2O}_{} + 14KI + 6H_2O.$$

It may also be termed di-iodamide. Collect the powder on a filter, divide it into four or five portions, and suffer them to dry in a quiet place. When dry, it explodes if touched even by a feather.

A chloride of nitrogen, Cl_3N, Cl_2HN, or a trichloramide may be formed by exposing sal-ammoniac to the action of chlorine gas. It is so violently explosive that none but expert chemists should attempt to prepare it.

(III) These derivative compounds are sometimes called *amides*, *imides*, and *nitriles*, as if formed from the radicals, NH_2 (amidogen), NH (imidogen), and trivalent nitrogen.

204. There are also derivatives containing both positive and negative radicals, which are called *alkalamides*. In some ammoniacal compounds the nitrogen appears to be pentavalent, as sal-ammoniac, NH_4Cl. If ammonia be added in excess to mercuric chloride, a white precipitate forms of the formula $\cdot N^{v}{}_2H'{}_4Hg''{}_2Cl'{}_2$ (dimercuric dichloramide). If ammonia be added to freshly precipitated mercurous chloride, black mercurous chloramide ($N^{v}H'{}_2Hg'{}_2Cl'$) forms. Both of these are alkalamide compounds.

COMPOUNDS OF NITROGEN AND OXYGEN.

205. There are five oxides of nitrogen, viz:

Protoxide, or nitrous oxide, N_2O.
Dioxide, or nitric oxide, N_2O_2; nitrosyl $(NO)'$.
Teroxide, or nitrous anhydride, N_2O_3.
Tetroxide, or nitric peroxide, N_2O_4; nitryl $(NO_2)'$.
Pentoxide, or nitric anhydride, N_2O_5.

The three highest oxides yield, with water, nitrous and nitric acids.

$N_2O_3 + H_2O = H_2O, N_2O_3$ or $2(HNO_2)$, nitrous acid.
$N_2O_4 + H_2O = HNO_2 + HNO_3$.
$N_2O_5 + H_2O = H_2O, N_2O_5$ or $2(HNO_3)$, nitric acid.

All of these oxides are obtained, in practice, either directly or indirectly from nitric acid.

206. The nitrates are formed by the oxidation of nitrogenous organic matters in the presence of strong bases. Potassium nitrate, or saltpeter, occurs native in India, and is also largely manufactured by the decomposition of other crude nitrates. Sodium nitrate, or Chili saltpeter, occurs in large beds in South America. Rain-water also contains traces of nitrates, which may come either from the oxidation of ammonia or from the action of atmospheric electricity.

207. Nitric acid is a monobasic acid, having the formula HNO_3; but we shall frequently find it convenient to use the binary formula H_2O, N_2O_5, which contains two molecules. It is obtained by distilling a nitrate with strong sulphuric acid.

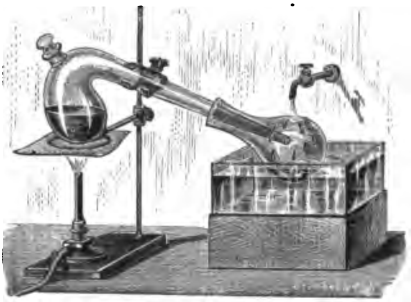

FIG. 63.

Exp. 133. — Heat equal weights of saltpeter and strong sulphuric acid, and collect the distillate in a receiver kept cool by water. Red fumes appear at the beginning of the process, but afterward a nearly colorless acid collects in the receiver. (Fig. 63).

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

When the distillation has ceased, and the retort has somewhat cooled, warm water may be added and the solution poured out. This yields, on evaporation, crystals of acid potassium sulphate. When half the quantity of sulphuric acid is used, the same reaction takes place in the first stages, but afterward the acid sulphate acts upon the saltpeter remaining to form normal potassium sulphate: $KHSO_4 + KNO_3 = K_2SO_4 + HNO_3$. This, however, is not advantageous, because the heat required is so great as to decompose a part of the nitric acid, and because the normal sulphate is less easily removed from the retort.

208. Physical properties. Pure nitric acid is a colorless, volatile liquid of the specific gravity 1.52. It solidifies at —55° C., and boils at 86° C. Nitric acid is usually more or less colored, owing to the absorption of the lower oxides of nitrogen, which are the products of its own partial decomposition. Red fuming nitric acid is the strong acid containing a considerable quantity of pernitric oxide. The ordinary *aqua fortis* contains from 30 to 60 per cent of nitric acid.

209. Chemical properties. Nitric acid is easily decomposed into water, oxygen, and a lower oxide of nitrogen. For this reason it is a powerful oxidizing agent.

Exp. 134.—Pour a little of the strongest nitric acid upon warm, powdered charcoal: the latter takes fire at once.

Exp. 135.—Drop a small pellet of phosphorus into the strongest nitric acid (placed at some distance from the operator, to avoid danger). It oxidizes, and frequently with such violence as to burst into flame. (Fig. 64).

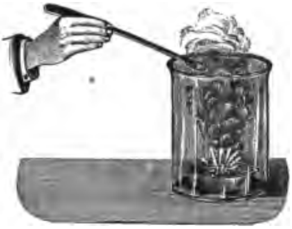

FIG. 64.

In like manner, sulphur and iodine, when heated with nitric acid, are converted to sulphuric and iodic acids. When nitric acid is poured upon the ordinary metals, it oxidizes them and is itself reduced to one of the lower oxides of nitrogen. The usual reactions may be illustrated by the following experiments.

Exp. 136.—Add nitric acid to tin foil. The latter is converted into white metastannic acid.

$$10(H_2O, N_2O_5) + 5Sn = Sn_5O_{10}, 10H_2O + 10N_2O_4.$$

The red fumes are nitric peroxide. If the white tin powder be mixed with slaked lime and gently warmed, ammonia will be given off, showing that a portion of the acid has been converted into H_3N.

Exp. 137.—Add strong nitric acid to copper clippings. A portion of the acid will be reduced to nitric oxide, and cupric oxide is formed: another portion unites with the cupric oxide to form blue cupric nitrate.

$$4(H_2O, N_2O_5) + 3Cu = 3(CuO, N_2O_5) + 4H_2O + N_2O_2.$$

This is the usual reaction with the metals. The nitric oxide is itself colorless, but is converted by contact with the air into red nitric peroxide. (See § **392**).

Nitric acid acts energetically upon organic matters. (1) It oxidizes them: thus, indigo is converted to isatin, and is thereby bleached. Starch and sugar are converted to oxalic acid. (2) It forms substitution products through the displacement of one or more atoms of hydrogen in the original compound by the radical nitryl $(NO_2)'$. Thus, benzole, C_6H_6, treated with strong nitric acid, becomes nitro-benzole, $C_6H_5(NO_2)$; phenol, or carbolic acid, C_6H_6O, yields tri-nitro-phenol, or picric acid, $C_6H_3(NO_2)_3O$. This latter substance is a permanent yellow dye. Nitric acid stains the skin and many other organic substances yellow, probably from the formation of picric acid.

Exp. 138.—Dip a skein of white silk thread into dilute nitric acid for a few minutes; then wash thoroughly with water. It will be colored permanently yellow.

The TESTS for free nitric acid are: (1) its bleaching power upon indigo; (2) the red fumes which it evolves when added to copper filings. The normal nitrates are all soluble in water. Nitric acid in combination is detected by warming the nitrates with strong sulphuric acid, and applying either of the above tests. (3) By adding to the mixture, when cold, a crystal of ferrous sulphate. A brownish color indicates the presence of nitric oxide. (Exp. 142).

210. Nitric anhydride, N_2O_5, may be obtained by very gently heating silver nitrate in a slow current of dry chlorine gas. It is a crystalline, unstable solid, which readily unites with water to form nitric acid.

211. The uses of nitric acid as an energetic oxidizing agent have already been indicated. Its substitution products, gun cotton and nitro-glycerine, are very powerful explosive compounds. Nitro-benzole is used as an artificial perfume, and as a material from which aniline can be made. Engravers employ the acid for etching designs upon copper and steel. It attacks all the metals except gold and the metals of the platinum group.

212. Aqua regia is a mixture of one part of nitric acid with three parts of hydrochloric acid. The two liquids react upon each other and liberate chloronitric gas and free chlorine.

$$H_2O, N_2O_5 + 6HCl = 2N\overset{\frown}{O}Cl_2 + 4H_2O + \overset{\frown}{Cl}_2.$$

A small quantity of chloronitrous gas, NOCl, is formed at the same time. The presence of the free chlorine renders aqua regia a solvent for gold and platinum. It should be prepared as wanted for use.

213. Nitrous oxide, N_2O, is prepared by gently heating ammonium nitrate. The salt readily melts and soon appears to boil, and is entirely decomposed into water and nitrous oxide.

$$NH_4, NO_3 \text{ heated} = 2H_2O + \overset{\frown}{N_2O}.$$

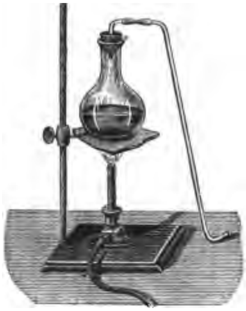

FIG. 65.

214. Physical properties. Nitrous oxide is a colorless, coercible gas, having a faint odor and a sweetish taste: sp. gr. 1.53. It liquefies at 7° C., under a pressure of 40 atmospheres, and solidifies at —100° C. The lowest temperature yet attained, —140° C., was produced by evaporating *in vacuo* a mixture of liquid nitrous oxide and carbon disulphide. The gas may be collected by displacement or over warm water. Water at 15° C. absorbs three-fourths of its volume of the gas.

215. The chemical properties of nitrous oxide resemble those of oxygen; but it does not form red fumes with nitric oxide.

Exp. 139.—Into jars of the gas, plunge (1) an ignited splinter of wood—it will burst into flame: (2) sulphur or phosphorus heated in a deflagrating spoon—the combustion will be very brilliant.

216. The physiological properties of the gas have given it the name of "laughing gas," because, when breathed in moderate quantity, it produces lively, stimulating effects. Breathed in large quantity, it produces temporary stupor, and hence is used as an anæsthetic in dental surgery. It is sometimes sold for this purpose in the liquid state, in wrought iron bottles.*

217. Nitric oxide, N_2O_2 or NO, is usually prepared by treating copper clippings or mercury with moderately dilute nitric acid. (Exp. 137). The gas may be collected over water, which absorbs the red fumes formed by the union of the NO with the air in the generating flask.

218. Physical properties. Nitrous oxide is a colorless, gas (sp. gr. 1.04), very slightly soluble in water, which liquefies under a pressure of 146 atmospheres.

219. Chemical properties. Nitric oxide may be considered as the free state of the monatomic radical nitrosyl (NO). It is one of the most stable of the nitrogen oxides. Ordinary combustibles do not burn in it; but phosphorus or carbon, when burning briskly, is able to decompose the gas and combine with its oxygen.

Exp. 140.—Into a jar of the gas, plunge a piece of dried phosphorus just ignited: it will be extinguished. Again introduce the phosphorus when in full combustion: it will burn as in oxygen.

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* CAUTION.—If the gas is to be used for inhalation, the ammonium nitrate should be free from sal-ammoniac, as, otherwise, it will be mixed with chlorine. If the nitrate is heated above 250° C., nitric oxide is formed, and sometimes explosive mixtures.

The special characteristic of nitric oxide is its strong attraction for free oxygen. It unites directly with it, producing deep red fumes which are chiefly nitric peroxide, N_2O_4, but mixed with nitrous anhydride, N_2O_3.

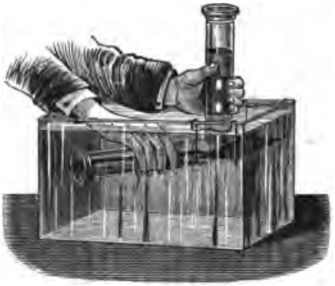

FIG. 66.

Exp. 141.—Fill a small jar with blue litmus water, and decant into it a pint of oxygen. Now add a pint of nitric oxide. Red fumes are formed which are soon absorbed by the water. Now add another pint of nitric oxide. If both the oxygen and the nitric oxide are pure, the gases will be completely absorbed by the water, showing that nitric peroxide is formed by the union of two volumes of nitric oxide with one of oxygen. The litmus becomes red.

Owing to this ready combination with oxygen, the actual taste, odor, and respirability of nitric oxide have not been ascertained.

Nitric oxide is readily absorbed by solutions of the ferrous salts, forming compounds such as $2FeSO_4, NO$.

Exp. 142.—Shake a little ferrous sulphate in a jar of the gas: a brown solution will be formed, which, on exposure to the air or on warming, soon becomes colorless.

220. Nitrous anhydride, N_2O_3, is best prepared by gently heating nitric acid with an equal weight of arsenious acid, and collecting the distillate in a U tube surrounded by a freezing mixture.

$$H_2O, N_2O_5 + As_2O_3 = H_2O, As_2O_5 + N_2O_3.$$

221. Physical properties. The nitrous anhydride thus obtained is a blue liquid, easily decomposed by heat, and forming with water at 0° C. a blue liquid which is nitrous acid, H_2O, N_2O_3 or HNO_2.

222. Nitrous acid is stable only at low temperatures or in very dilute solutions. When heated, it decomposes into nitric oxide, which escapes with effervescence, and into nitric acid and water, which remain in the solution.

The alkaline nitrites are produced by heating the alkaline nitrates to redness. Oxygen is given off; a mixture of free alkali and nitrite remains.

Exp. 143.—Heat potassium nitrate in a crucible until a portion, removed on the end of an iron rod, gives a strong alkaline reaction. Then pour the fused mass on a dry stone, and, when cooled, preserve the potassium nitrite in stoppered bottles.

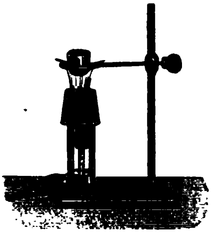

FIG. 67.

Nitrous anhydride is disengaged when a nitrite is treated with a dilute acid. It is, however, almost immediately decomposed into nitric oxide and nitric acid. The acidulated solutions of the nitrites act:

(I) As reducing agents.

Exp. 144.—To a solution of potassium permanganate, add a few drops of sulphuric acid and then a solution of potassium nitrite. The red color disappears: MnO, SO_3 is formed.

(II) As oxidizing agents.

Exp. 145.—To a dilute indigo solution, add a solution of potassium nitrite and then a few drops of sulphuric acid. The indigo is changed to isatin and bleached.

Exp. 146.—To a solution of potassium iodide, add the nitrite and acidulate. The potassium is oxidized and the iodine set free. The iodine may be detected by starch paste, or dissolved out of the aqueous solution by carbonic disulphide.

TESTS.—The above reactions are also tests for nitrous acid. The nitrites are distinguished from the nitrates by giving, with ferrous salts, a brown discoloration without the addition of an acid.

223. When ammonia is burned in the air it is decomposed, and both of its constituents unite with oxygen — the hydrogen to form water, the nitrogen to form nitrous anhydride or some other oxide of nitrogen.

Exp. 147.—Shake copper filings, with a little strong aqua ammonia, in a large flask. White fumes will be produced, the liquid will become blue, and will be found to contain oxide of copper and nitrite of ammonia.

Exp. 148.—Suspend a highly heated coil of thin platinum wire in a flask containing a little strong aqua ammonia. Thick, white clouds of ammonium nitrite are formed, and sometimes red vapors of nitrous anhydride. If a tube delivering oxygen be passed into the flask, the action will be more energetic. The spiral will glow for some time, the red fumes will be more abundant, and little explosions rapidly succeed one another.

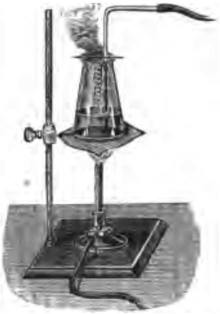

FIG. 68.

224. Nitric peroxide, N_2O_4 or NO_2, has already been mentioned as forming the greater part of the red fumes which are produced by the action of oxygen upon nitric oxide.

225. Physical properties. It is possible to condense these fumes into a crystalline solid which melts at —9° C., or to a volatile, almost colorless liquid whose color changes, as the temperature rises, from a greenish yellow to yellow, and then to orange. At 22° C. it boils and forms red vapors, which may become so dark as to be almost opaque. These vapors are irrespirable, and have a pungent, suffocating odor.

226. Chemical properties. Although ordinary combustibles are extinguished by nitric peroxide, it is an energetic oxidizing agent. Its use in converting sulphurous to sulphuric acid has already been mentioned. In the presence of water it is decomposed into nitrous and nitric acids, with the formation of a liquid whose color varies from green to blue, according to the proportion of nitrous acid and unaltered nitric peroxide present. The same coloration is frequently observed when silver, mercury, or lead is dissolved in nitric acid, sometimes leading the novice to suspect the presence of copper.

Nitric peroxide acts as the free molecule of the monatomic radical *nitryl*, NO_2, which is capable of replacing hydrogen in many organic compounds.

PHOSPHORUS.

227. Phosphorus is never found uncombined in nature, but is very widely and abundantly diffused in the form of phosphates. Calcium phosphate, the chief source of this element, is found in guano, coprolites, and in apatite. It is also found in small quantities in all arable soils, whence it is taken up by plants and accumulated in their seeds. The animals which feed upon these seeds assimilate it, and hence it forms a part of almost every solid and liquid in the bodies of animals. The bones of oxen contain nearly 58 per cent of calcium phosphate and 2 per cent of magnesium phosphate. When bones are burnt they leave a white and friable ash, which is impure tri-calcium phosphate, $3CaO, P_2O_5$.

228. Preparation. Phosphorus and its compounds are obtained from this "bone ash."

(1) The ground bones are digested for some hours with two-thirds their weight of strong sulphuric acid and six times their weight of water. An insoluble calcium sulphate and a soluble monocalcic phosphate, or "superphosphate of lime," are formed.

$$3CaO, P_2O_5 + 2(H_2O, SO_3) = 2(CaOSO_3) + CaO, 2H_2O, P_2O_5.$$

(2) The calcium sulphate is removed by filtration. The solution is then evaporated to a syrup, and is then mixed with one-fourth

of its weight of charcoal, and heated to redness. The monocalcic phosphate is converted into calcium meta-phosphate, CaO, P_2O_5.

$$CaO, 2H_2O, P_2O_5 \text{ heated} = CaO, P_2O_5 + 2\overbrace{H_2O}.$$

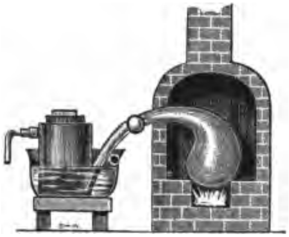

FIG. 69.

(3) On distilling this mixture of charcoal and calcium metaphosphate in a retort, phosphorus is set free, passes over in vapor, and may be condensed under water. The calcium retains enough of the acid to reconvert it into tricalcic phosphate.

$$3(CaO, P_2O_5) + 10C = \\ 3CaO, P_2O_5 + 10\overbrace{CO} + \overbrace{P_4}.$$

(4) The crude phosphorus thus prepared is purified by melting it under water containing a little chromic acid. It is then run into a horizontal tube surrounded by cold water, by which it is chilled, and is then drawn out in solid sticks.

229. Physical properties. Pure phosphorus, when first made, is an almost colorless, translucent solid: sp. gr. 1.82. It melts at 44° C., and boils in closed vessels at 290° C. The vapor density at 500°, referred to the hydrogen unit, is 62.1, which is double its atomic weight; from which it appears that the atom of phosphorus occupies only half the volume of the hydrogen atom, or that the molecule of phosphorus contains four atoms.

Phosphorus is somewhat soluble in turpentine and in essential and fixed oils. It is readily dissolved by carbonic disulphide. If this solution be evaporated in an atmosphere of carbonic anhydride, the phosphorus may be obtained in dodecahedral crystals.

230. Chemical properties. Phosphorus exposed to the air at ordinary temperatures undergoes a slow combustion, and is feebly luminous in the dark. Hence its name, which means the light-bearer (φῶς, φέρω). It is extremely inflammable, taking fire in the air a little above its melting point. (Compare Exp. 48). On this account it is kept under water, and should be handled with great caution.

Phosphorus combines readily with many of the elements. (Exps. 10, 74, 88). Its compounds with the metals are called phosphides or phosphurets. Owing to the strong affinity of phosphorus for oxygen, it is an energetic reducing agent, and is capable of precipitating copper, lead, and some other metals from solutions of their salts.

Exp. 149.—Place a pellet of phosphorus in a solution of silver nitrate. In a few days it will be covered with metallic silver.

231. Phosphorus is capable of assuming several allotropic states, the most remarkable of which is the red, or amorphous, phosphorus. This may be prepared by heating ordinary phosphorus in an atmosphere of carbonic anhydride, at a temperature of 230° to 235° C., for thirty hours. The two modifications differ so much that we should suppose them to be different elements if we could not convert one into the other. The red phosphorus has a specific gravity of 2.14, is insoluble in carbon disulphide, does not inflame by friction, is unaltered in the air, and is not poisonous. If heated to 260° C., it is converted into ordinary phosphorus and bursts into a flame.

Ordinary phosphorus is very poisonous. Cases have occurred in which children have been poisoned by sucking the phosphorus combination on the tips of matches. Its vapor sometimes causes a necrosis of the jaw-bone. The best antidote is calcined magnesia.

232. Uses of phosphorus. "Lucifer matches" are made by tipping small wooden sticks with sulphur or paraffine, to convey the flame, and, afterward, with a composition containing ordinary phosphorus, glue, and an oxidizing substance like saltpeter or potassium chlorate. These matches take fire when rubbed on any rough surface.

"Safety matches" are tipped with a mixture of antimonous sulphide and potassium chlorate. These do not readily take fire by friction, but inflame when they are rubbed on a surface containing amorphous phosphorus, manganese dioxide, and fine sand.

Various attempts have been made to manufacture matches without phosphorus. Good matches have been made with a composition of potassium chlorate and lead hyposulphite.

A very common rat poison is made from ordinary phosphorus mixed with flour paste.

233. Tests. Free, ordinary phosphorus may be detected by its luminosity in the dark; phosphorus in combination, by heating the dry powder which contains it in a thin glass tube with a small bit of magnesium or sodium. On breaking the tube and adding water, the odor of hydrogen phosphide will be perceived, and frequently, also, its flame. Any one of its allotropic forms may be detected by oxidizing it to phosphoric acid, and applying the test for that body.

234. Compounds of phosphorus and hydrogen. Three of these compounds are known: (1) a solid phosphide, HP_2(?); (2) a spontaneously inflammable liquid phosphide, H_2P; and (3) gaseous phosphide, H_3P, generally called phosphuretted hydrogen.

235, Phosphuretted hydrogen is usually obtained by heating phosphorus in a strong alkaline solution.

Exp. 150.—Place in a small flask a few slices of phosphorus, and fill the flask with a strong solution of caustic potash. The evolution tube should dip under warm water. On gently heating the flask, bubbles of the gas mixed with free hydrogen escape into the air, and spontaneously inflame, with the production of beautiful white rings of phosphoric anhydride. (Fig. 70).

$$P_4 + 3H_2O + 3KHO = 3(KPH_2O_2) + H_3P.$$

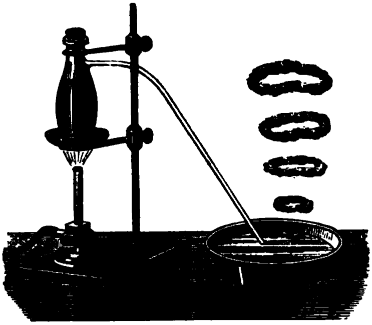

FIG. 70.

236. Physical properties. Phosphuretted hydrogen is a colorless, coercible gas: sp. gr. 1.19. It has an offensive odor, being the same as that evolved by putrid fish.

237. Chemical properties. The gas is not spontaneously inflammable. This property is given it by the presence of a small quantity of the liquid phosphide of hydrogen, and is lost when the gas is passed through a freezing mixture, or by admixture with the oil of turpentine.

When the gas is passed into solutions of copper, a black precipitate of copper phosphide is formed. This phosphide, heated in a solution of potassium cyanide, evolves self-lighting phosphuretted hydrogen.

TESTS.—Its odor is very characteristic. Salts of silver and gold are reduced to the metallic state by this gas.

238. The terchloride, PCl_3, forms when phosphorus is burned in chlorine; or, if the chlorine be in excess, the pentachloride, PCl_5. Both are decomposed by water, the latter forming an oxychloride, $POCl_3$. Phosphorus also combines with bromine, iodine, and sulphur. These compounds are of great importance in organic chemistry in forming "substitution compounds."

239. The oxygen compounds of phosphorus. Besides a suboxide of phosphorus, P_4O, which is imperfectly known, two anhydrides of phosphorus have been obtained as bulky, white, amorphous powders, by burning phosphorus in dry air. If the combustion is very slow, the greater part of the product is phosphorus anhydride,. P_2O_3: if the combustion is very rapid, the product is almost pure phosphoric anhydride, P_2O_5. Both of these anhydrides absorb moisture with the greatest avidity, and combine with three molecules of water to form the corresponding acids, to which the following formulæ have been given:

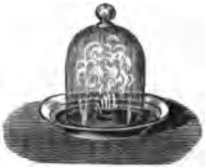

FIG. 71.

$$3H_2O, P_2O_3, \text{ phosphorous acid, } H_2, PHO_3.$$
$$3H_2O, P_2O_5, \text{ phosphoric acid, } H_3, PO_4.$$

There are also other acids of phosphorus,—two obtained by the partial dehydration of phosphoric acid, viz:

$$2H_2O, P_2O_5 = \text{pyrophosphoric acid, } H_4, P_2O_7.$$
$$H_2O, P_2O_5 = \text{metaphosphoric acid, } H, PO_3.$$

Hypophosphorous acid, H, PH_2O_2, for which no corresponding anhydride is known, is another. The basicity of these acids varies from one to four, and is expressed by the hydrogen at the left of their formulæ.

240. The alkaline hypophosphites are formed by boiling phosphorus in alkaline solutions, as in Exp. 150. The aqueous solution of hypophosphorous acid is obtained by decomposing barium hypophosphite with sulphuric acid.

The acid and the alkaline hypophosphites are energetic reducing agents. They form, with silver nitrate, a white precipitate which quickly becomes black, metallic silver. When the dry salts are heated, they are converted into phosphates, and evolve phosphuretted hydrogen.

241. An impure phosphorous acid is obtained by exposing sticks of phosphorus to the action of moist air. The solution readily absorbs oxygen, and is changed to phosphoric acid. It reduces silver nitrate like the hypophosphites, but less energetically.

242. Orthophosphoric acid is prepared by oxidizing phosphorus with nitric acid.

$$5(H_2O, N_2O_5) + 4H_2O + P_6 = 3(3H_2O, P_2O_5) + 10NO.$$

This solution evaporated at a gentle heat forms a syrupy liquid, from which, by evaporating *in vacuo*, hard, transparent crystals may be obtained, called orthophosphoric acid. The formula is $3H_2O, P_2O_5$ or H_3PO_4. This is the ordinary phosphoric acid, and is tribasic.

If the solution of orthophosphoric acid be heated to 215° C., one equivalent of water is expelled and *pyro-phosphoric acid* is formed, which has the formula, $2H_2O, P_2O_5$ or $H_4P_2O_7$, and is tetrabasic.

If the solution is further evaporated in a platinum vessel until white fumes begin to be given off, a transparent, glassy mass is obtained, which is the *glacial* phosphoric acid of commerce, or *meta-phosphoric acid.* Its formula is H_2O, P_2O_5 or HPO_3, and it is monobasic. Metaphosphoric acid will coagulate the albumen found in the white of egg, and will give a white, gelatinous precipitate of $AgPO_3$ when it is added to silver nitrate.

The other phosphoric acids do not coagulate albumen, nor do they precipitate silver nitrate. If, however, a few drops of soda be added to their solutions, the pyrophosphate which is formed will precipitate as white pyrophosphate of silver, $Ag_4P_2O_7$; the orthophosphate, as yellow orthophosphate of silver, Ag_3PO_4.

Metaphosphoric acid forms but one class of salts; but both the ortho- and pyro-phosphoric acids form a great variety of salts, inasmuch as their hydrogen may be replaced by one or more metals, in accordance with their atomicity,—a monad metal replacing one hydrogen atom; a dyad, two, etc.

Exp. 151.—Take the solution of superphosphate of lime, prepared by treating bone ash with sulphuric acid, and add sodium carbonate until the liquid is faintly alkaline. Filter off the calcium carbonate which forms, and evaporate the solution till a drop of it placed on a watch glass readily crystallizes. On cooling the solution, crystals of di-sodium phosphate will form: $Na_2HPO_4, 12H_2O$.

Exp. 152.—Mix a portion of the preceding solution with caustic soda, and evaporate as before. The crystals formed are tri-sodium phosphate: $Na_3PO_4, 12H_2O$.

Exp. 153.—Mix another portion with orthophosphoric acid until it no longer precipitates calcium chloride, and then evaporate. On evaporation, crystals of monosodium phosphate, NaH_2PO_4, H_2O, are formed. All these salts give, with silver nitrate, the same precipitate of Ag_3PO_4.

243. If these three sodium salts be heated until they become dry, the water of crystallization will be expelled.

On heating them to redness, the first will lose a molecule of water and become sodium pyrophosphate.

$$2(Na_2HPO_4) \text{ ignited} = Na_4P_2O_7 + H_2O.$$

The second will suffer no further change; the third will lose two molecules of water and become sodium metaphosphate.

$$NaH_2PO_4 \text{ ignited} = NaPO_3 + H_2O.$$

If these residues are again dissolved in cold water. and a solution of silver nitrate added, they will yield: (1) white $Ag_4P_2O_7$, (2) yellow Ag_3PO_4, (3) white, gelatinous $AgPO_3$—showing the production in the first of pyrophosphoric acid, in the third of metaphosphoric acid: the orthophosphoric acid of the second remaining unaltered, because no part of its base was volatile.

If these silver precipitates be suspended in water, and a stream of hydrogen sulphide be passed through the liquid, black, insoluble silver sulphide will be formed, and the solutions of the different phosphoric acids may be obtained.

The meta- and pyro-phosphoric acids are converted into the orthophosphoric acids by prolonged boiling with water.

244. Tests. Orthophosphoric acid is estimated by adding to its solution a mixture of magnesium chloride, ammonium chloride, and ammonia. There precipitates white Mg'', NH_4PO_4, which becomes, on ignition, $Mg_2P_2O_7$. The acids are distinguished from one another by their reactions with silver nitrate and albumen.

245. Uses. Phosphoric acid is used in calico printing. The superphosphate of lime is used as a fertilizer.

ARSENIC.

246. Arsenic is found native; in combination with sulphur, as realgar, As_2S_2, and orpiment, As_2S_3; but more frequently in combination with the metals, as arsenides. The chief sources of arsenic and its compounds are iron arsenide, $FeAs_2$, and arsenical pyrites, FeS_2FeAs_2. It is widely diffused, being found in small quantity in many metallic sulphides and the products obtained from them.

247. Preparation. The element arsenic is obtained from arsenical pyrites by roasting it in horizontal tubes. The arsenic is volatilized, and is then condensed in the cooler portions of the tubes. It is also obtained by heating arsenious anhydride with charcoal. This process may be illustrated by one of the methods employed in testing.

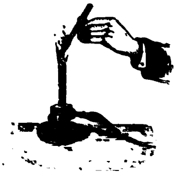

FIG. 72.

Exp. 154.—Introduce into a small tube of hard glass a little dry arsenious oxide, and place above this a few splinters of charcoal. First heat the coal to ignition, and then the arsenious oxide. As its vapor passes through the coal it is reduced, and condenses as a shining black ring on the colder portion of the tube.

248. Physical properties. Arsenic is a brittle solid of a steel-gray color and metallic luster. It volatilizes without fusing, at 180° C., and emits a peculiar, garlic-like odor. Its vapor density is double its atomic weight, and hence, like phosphorus, its molecule contains four atoms.

249. Chemical properties. Arsenic oxidizes in moist air, especially when heated. At a red heat it burns with a bluish white flame, and evolves white clouds of arsenious oxide. It is spontaneously combustible in chlorine, and combines readily with bromine, iodine, and sulphur.

When powdered arsenic is exposed to the air it forms a black powder which is sold under the name of *cobalt*, or "fly poison." All the compounds of arsenic are irritant poisons. The best antidote is prepared by precipitating ferric chloride with caustic magnesia.

250. Arsenetted hydrogen, H_3As, derives its chief interest from the fact that its production allows the detection of any soluble form of arsenic, even in very minute quantities. It is a colorless, coercible gas: sp. gr. 2.7. It has an alliaceous odor, and, even when largely diluted, is exceedingly poisonous.

251. Chemical properties. It burns in the air with a livid flame, producing arsenious anhydride and water. It is decomposed at a red heat into hydrogen and arsenic. When passed into a solution of silver nitrate, it precipitates metallic silver and forms arsenious acid. $6AgNO_3 + H_3As + 3H_2O = 6\underset{\vee}{Ag} + 6HNO_3 + H_3AsO_3$.

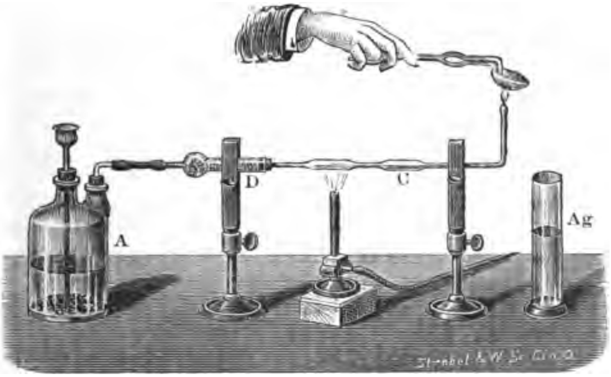

FIG. 73.

252. Marsh's test for arsenic is conveniently applied by the apparatus shown in Fig. 73.

Exp. 155.—A is a two-necked bottle; D, a drying tube containing potassium hydrate and calcium chloride; C, a tube of hard glass contracted at one or two points and terminating in a vertical jet; Ag, a solution of silver nitrate.

To study the properties of the gas, let a handful of granulated zinc be put in the bottle and then covered with dilute sulphuric acid. After the air has been expelled from the apparatus, the jet of hydrogen may be lighted. It should burn with an almost colorless flame.

Now pour a little of a solution of arsenious acid in boiling water down the funnel tube. Notice, (1) the burning jet will change its color to a bluish white; (2) a cold porcelain plate held in the flame will acquire a dark, metallic spot; (3) obtain several of these, and, while doing so, heat the tube, C, in one or more places by the full flame of a good lamp. The white color will disappear from the burning jet, and a ring of metallic arsenic be formed in the tube a little beyond the flame of the lamp. Little or no deposit will then be formed on the plate. (4) Again remove the lamp and turn the jet into the silver solution. Black, metallic silver will be precipitated. The silver solution should be quite dilute at first, and, if much arsenic is present, more silver nitrate added from time to time.

To understand these reactions, we may suppose the arsenious acid to have been reduced by the nascent hydrogen to arsenic. A part of this remains as a black deposit on the zinc, and another part combines with another portion of the hydrogen, and escapes as arsenetted hydrogen. The white fumes which color the flame are arsenious acid. The black deposits are arsenic, produced by its decomposition. The silver solution will contain arsenious acid in the presence of free nitric acid.

We may now apply confirmatory tests. To the spots on porcelain, (1) add a fresh solution of an alkaline hypochlorite—the spots will disappear: (2) add ammonium sulphide—it will very slowly change to yellow arsenious sulphide. Now make several closed tubes of the tube, C. (3) Heat one of these tubes, and notice that the ring may be driven from one part to another. (4) Add a little nitric acid—the black ring will be dissolved. Apply any of the tests for arsenic acid to the solution. (5) Filter the silver solution, and carefully add just enough ammonia to neutralize the free nitric acid. If any undecomposed silver nitrate remains, a yellow precipitate of silver arsenite, Ag_3AsO_3, will form; or it will form on the addition of more silver nitrate.* Finally, try **Exp. 156.**

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* A more expeditious method consists in the substitution of sodium amalgam for the zinc: no acid is required. Slips of paper moistened with silver nitrate, and held over the gas which escapes, will blacken if only $\frac{1}{100000}$ grain of arsenic is present.

253. If all of these tests can be obtained, there can be little doubt of the presence of arsenic. In toxicological examinations others must also be had. So, also, the materials used must be tested, to determine that no arsenic is present in them.

This is done by subjecting the hydrogen which is at first evolved to the same tests for at least fifteen minutes before adding the suspected substances. It should be added that these substances must be previously freed from organic matters. If the liquid contains free nitric acid, a solid arsenetted hydrogen, H_2As, is formed in the flask.

254. The oxygen compounds of arsenic. Arsenic yields two anhydrides and a series of acids, which correspond to phosphorous and phosphoric acids.

ANHYDRIDES.		ACIDS.	
Arsenious anhydride,	As_2O_3.	Arsenious acid,	$H_3As\ O_3$.
Arsenic anhydride,	As_2O_5.	Ortho-arsenic acid,	$H_3As\ O_4$.
		Pyro-arsenic acid,	$H_4As_2O_7$.
		Meta-arsenic acid,	$H\ As\ O_3$.

255. Arsenious anhydride, As_2O_3, is formed when arsenic is burned in air. It is prepared in large quantities by roasting arsenical pyrites in muffle furnaces through which the air is allowed to pass, and is condensed as a fine, white powder in large chambers.

Exp. 156.—Heat the arsenical deposit in a portion of the tube, C (Fig. 73), leaving both ends open to admit air. The black ring will volatilize and again condense to white, crystalline As_2O_3.

256. Physical properties. Arsenious anhydride is a white, tasteless solid: sp. gr. 3.7. The powder which is sold under the name of white arsenic, or ratsbane, is its usual form; but it can also be obtained by fusion as a glassy mass, which soon becomes opaque like porcelain. By boiling for several hours, 100 parts of water can dissolve 11.5 parts of the anhydride. The solution, on cooling, deposits 9 parts as octahedral crystals, leaving

2.5 parts dissolved. It is rather more soluble in hydrochloric acid; but, *on boiling with hydrochloric acid, arsenious chloride,* $AsCl_5$, *is formed and volatilizes.*

257. Chemical properties. No definite hydrate of the acid has been obtained. It forms, however, with the metals, well marked arsenites. Fowler's solution is potassium arsenite, made by boiling the anhydride in a solution of potassium carbonate. Arsenious acid acts as a reducing agent when heated with nitric acid and other bodies rich in oxygen, and is itself converted to arsenic acid, As_2O_5. If heated with charcoal, phosphorus, and similar reducing agents, it is reduced to the element arsenic, and acts as an oxidizing agent.

258. Uses. As an oxidizing agent, it is used in the manufacture of glass to convert ferrous to ferric oxide. It is also used in the manufacture of shot and of several green pigments. An arsenical soap, containing arsenious acid and camphor, is used by naturalists for preserving the skins of animals.

TESTS.--Neutral solutions of the alkaline arsenites give a green precipitate (Scheele's green) with cupric sulphate, and a yellow precipitate with silver nitrate.

Reinch's test is made by acidulating the acid or its compounds with hydrochloric acid, and heating the mixture gently after the addition of a bright copper strip. After a little while, a steel-gray coating of Cu_5As_2 is formed.

259. Physiological properties. Although two decigrammes of arsenious acid are sufficient to destroy life, it is possible gradually to accustom the human body to daily doses of three decigrammes, or even more. As a medicine, small doses of arsenious acid are used in intermittent fevers and in skin diseases.

260. Arsenic acid is prepared by oxidizing arsenious anhydride with nitric acid. On evaporating the solution to a syrup, deliquescent crystals of $3H_2O, As_2O_5 + H_2O$ are deposited in rhomboidal laminæ. These crystals, heated to 100° C., lose the water of crystallization and become the tribasic acid ($3H_2O, As_2O_5$): at 160° C., pyro-arsenic acid ($2H_2O, As_2O_5$); at 260° C., meta-arsenic acid (H_2O, As_2O_5); at a dull red heat, arsenic anhydride (As_2O_5), which decomposes at a full red heat. All these bodies dissolve in water and yield the trihydrate.

261. Properties. Arsenic acid appears to be less poisonous than arsenious acid, but its acid properties are more marked. It is largely used in calico printing and in the manufacture of aniline colors.

TESTS.—Arsenic acid yields a brick-red silver arseniate, Ag_3AsO_4, with silver nitrate. It forms many precipitates which closely resemble those of the tribasic phosphoric acid. The ammonio-magnesian mixture gives white $Mg''NH_4AsO_4$, which is used for the quantitative determination of arsenic.

Arsenic acid and its salts are reduced by boiling with sulphurous acid. They then yield the tests for arsenious acid.

All compounds of arsenic in acid solutions yield, with sulphuretted hydrogen, a yellow precipitate of As_2S_3; but it must be noted that with the higher compounds the precipitate forms slowly, and generally only after heating.

262. The principal sulphides of arsenic are realgar, or red orpiment, As_2S_2; yellow orpiment, or king's yellow, As_2S_3; and the penta-sulphide, As_2S_5. The first two are found native, but all are prepared artificially.

Realgar is used in pyrotechny. One part of realgar mixed with 3.5 parts of sulphur and 14 of saltpeter yields a beautiful white flame (Indian fire).

The other two are interesting because they form soluble compounds with the alkaline sulphides. These compounds are sulpho-salts which are analogous to the oxy-salts, and, hence, As_2S_3 is sometimes called sulpharsenious acid, and As_2S_5, sulpharsenic acid.

Sulpharsenious acid is the yellow precipitate formed by passing H_2S into an acidified solution of the arsenites. The same compound mixed with free sulphur is formed by treating arsenic acid with H_2S. It forms slowly in cold solutions; more rapidly on boiling.

If, however, sodium arseniate is saturated with H_2S, a soluble sulpharseniate of sodium, $2Na_2S, As_2S_5$, forms. Hydrochloric acid added to this solution precipitates the yellow As_2S_5.

Either of these sulpho-acids is soluble in ammonium carbonate.

ANTIMONY.

263. Antimony is found native, but generally in combination with oxygen, sulphur, and certain metals.

264. Preparation. The antimony of commerce is obtained from stibnite, Sb_2S_3, by fusing it with scrap iron: $Sb_2S_3 + 3Fe = 3FeS + 2Sb$. The product is crude antimony, which is purified by a second fusion with sodium carbonate. Pure antimony may be obtained for experimental purposes by heating tartar emetic to bright redness in a covered crucible.

265. Physical properties. Antimony is a brittle, crystalline metal of lustrous, bluish white color: sp. gr. 6.7. It melts at 450° C., and volatilizes at red heat. The antimony which is obtained by electrolysis sometimes has the curious property of exploding when heated or struck.

266. Chemical properties. Antimony is not oxidized in air at ordinary temperatures, but, when heated above its melting point, oxidizes rapidly, and, at a red heat, burns with a white flame.

Exp. 157.—Heat a lump of the *pure* metal on charcoal before the blowpipe. Dense, white fumes will be given off. These are antimonious oxide, Sb_2O_3. Allow the molten mass to cool before it is completely burnt away. It will become covered with a crystalline network of the same oxide.

267. Uses. Antimony forms alloys with most of the heavy metals, rendering them harder, more brittle, and frequently suitable for forming sharp casts. Among these are type metal (Sb and Pb), Brittania metal, and pewter (Sn and Sb).

268. The compounds of antimony.—(I) **The chlorides.** Finely powdered antimony takes fire spontaneously in chlorine gas, forming either $SbCl_3$ or $SbCl_5$, according as the antimony or chlorine is in excess. Hence, if a slow current of chlorine be passed through a tube containing antimony, antimonious chloride, $SbCl_3$, will be formed. This condenses as a soft, gray solid known as the butter of antimony. It is also formed when antimonious sulphide is boiled with hydrochloric acid.

If chlorine gas be passed over antimonious chloride, a yellowish, volatile liquid forms, which is antimonic chloride, $SbCl_5$.

(II) **Oxides.** Both of these chlorides are decomposed when added to a large quantity of water. The first yields a white powder, the oxychloride of antimony ($SbCl_3, Sb_2O_3$); the second, white metantimonic acid ($2H_2O, Sb_2O_5$). If these two precipitates are gently heated, they form antimonious oxide, Sb_2O_3, and antimonic oxide, Sb_2O_5. When either of these is strongly heated, a yellow powder is formed which is probably a mixture of both: $Sb_2O_3, Sb_2O_5 = 2Sb_2O_4$.

(III) **Acids.** These oxides of antimony dissolve in alkaline solutions to form antimonites and antimonates. They may also be obtained as antimonious acid, $H_2O, Sb_2O_3 = HSbO_2$, and antimonic acid, $H_2O, Sb_2O_5 = 2(HSbO_3)$. This last corresponds to metaphosphoric acid. There is also a tetrabasic acid, $H_4Sb_2O_7$, which is called metantimonic acid. It corresponds to pyrophosphoric acid. Potassium metantimoniate is sometimes used in testing for sodium.

269. Antimonious oxide acts not merely as an acid, but also as a basic anhydride. It readily dissolves in tartaric acid to form antimonious tartrate. It also dissolves readily in acid potassium tartrate, and thereby forms the well-known tartar emetic:

$$Sb_2O_3 \text{ or } (SbO)_2O + 2(KH, C_4H_4O_6) = 2(K, SbO, C_4H_4O_6) + H_2O.$$

In these cases we may suppose it to be represented by the radical antimonyl $(SbO)'$.

270. Tests. When a stream of hydrogen sulphide is passed through acidulated solutions containing the compounds of antimony, sulphides of antimony are formed which are sulpho-acids similar to those of arsenic. The antimonic compounds yield a yellowish red antimonic sulphide, Sb_2S_5; the antimonious compounds, orange red antimonious sulphide, Sb_2S_3, soluble in ammonium sulphide. Both of these dissolve in hot hydrochloric acid as chlorides, which are decomposed by a large quantity of water—$SbCl_5$ yielding $H_4Sb_2O_7$; $SbCl_3$, a white oxychloride, $SbCl_3$, Sb_2O_3, or $3SbOCl$, soluble in tartaric acid.

Marsh's test yields, with the compounds of antimony, an odorless, antimonetted hydrogen, H_3Sb, which gives reactions similar to those observed with arsenic. They are, however, easily distinguished. (1) The metallic deposits are darker and are less volatile than those of arsenic. (2) They are insoluble in alkaline hypochlorites which do not contain free chlorine. (3) Gently warmed with nitric acid, they are oxidized but not dissolved. The antimonious oxide formed yields black Ag_4O, with neutral silver nitrate and ammonia. (4) They are readily soluble in ammonium sulphide. (5) The deposit in the silver solution is black Ag_3Sb, silver antimonide; hence, if any precipitate forms in the solution when filtered on the addition of ammonia, it is the oxide of silver.

Reinsch's test yields purple copper antimonide.

271. Uses. Antimonious chloride is used for bronzing gun barrels. Antimonious sulphide is used in the preparation of blue signal lights (Bengal light). Tartar emetic is used in medicine.

BISMUTH.

272. Bismuth is found chiefly in the metallic state, and is freed from its earthy impurities by heating the ore in iron cylinders which are fixed in an inclined position over a furnace. (Fig. 74). The bismuth melts at 264° C., and runs out at the lower ends of the tubes into iron vessels.

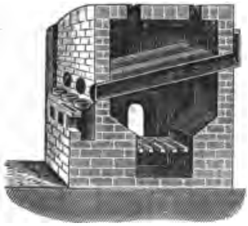

FIG. 74.

273. Physical properties. Bismuth is a brittle metal of a reddish luster: sp. gr. 9.8. It may be obtained in beautiful, rhombohedral crystals by melting several pounds of it, allowing it to cool till a crust has formed on its surface, and then pouring out the metal which still remains molten. The crystals will be found lining the interior of the crucible. The metal expands $\frac{1}{32}$ in solidifying. It is the most highly dia-magnetic substance known.

274. Chemical properties. Bismuth does not oxidize in the air at ordinary temperatures. It burns when strongly heated in the air with a bluish flame, forming yellow fumes of bismuthous oxide, Bi_2O_3. It unites directly with chlorine, bromine, iodine, and sulphur. It readily dissolves in nitric acid, forming the bismuthous nitrate, $Bi_2O_3, 3N_2O_5$ or $Bi(NO_3)_3$.

275. Uses. Bismuth is used, together with antimony, in the construction of thermo-electric batteries. Its presence in alloys has a wonderful influence in lowering the melting point. Rose's fusible metal melts at 94° C. It is composed of two parts of bismuth and one each of lead and tin, or very nearly Bi_2PbSn_4. This is valuable for taking impressions of dies, inasmuch as it expands on cooling, and reproduces the faintest lines with accuracy.

276. The compounds of bismuth.—(I) **Oxides.** If bismuthous nitrate is dissolved in a small quantity of water, and added to an excess of potassium hydrate, bismuthous hydrate precipitates as $3H_2O, Bi_2O_3$ or H_3BiO_3. This body becomes, on ignition, Bi_2O_3, bismuthous oxide. It seems also to enter into compounds as the monatomic radical $(BiO)'$, to form salts which are known as basic or sub-salts.

Bismuthic acid, H_2O, Bi_2O_5 or $HBiO_3$, is formed by passing chlorine gas through a hot potash solution which contains bismuthous hydrate in suspension. Its acid powers are weak and its salts are of no importance.

If bismuthous nitrate is thrown into a large quantity of water, it precipitates a basic or sub-nitrate of bismuth, Bi_2O_3, N_2O_5 or $(BiO)'NO_3$, also known as flake white.

(II) **Chlorides.** If the nitrate is poured into a solution of sodium chloride, an oxychloride of bismuth, $BiCl_3, Bi_2O_3 = 3BiOCl$, or "pearl white," precipitates. This dissolves in hydrochloric acid to bismuthous chloride, $BiCl_3$, and again precipitates on the addition of water. The formation of these basic bodies by water is characteristic of bismuth. Unlike the similar compounds of antimony, they are insoluble in tartaric acid.

(III) **Salts.** Bismuthous carbonate, $(BiO)_2CO_3$, is formed by decomposing bismuthous nitrate by an excess of an alkaline carbonate. This salt and the basic nitrate are used in medicine. Pearl white is used as a cosmetic.

TESTS.—The salts of bismuth are sufficiently characterized by their decomposition with water. They form, with soluble sulphides, black precipitates which are bismuthous sulphide, Bi_2S_3.

Recapitulation.

Review sections 190, 191, and 193.

This group contains all the pentad elements. Although the members of the group exhibit marked differences, they also exhibit a marked gradation of properties, which will be best shown by dividing them into sub-groups, as follows:

I	II	III	IV	V
N 14	P 31	P 31	P 31	As 75
P 31	V 51	As 75	Sb 122	Sb 122
V 51	As 75	Sb 122	Bi 210	Bi 210

Note that the atomic weight of the middle element in each of these sub-groups is very nearly the mean of the other two. In each of these sub-groups the middle element also exhibits more or less resemblance to the first and third, and may be said, in a general sense, to form a connecting link between them.

Among the numerous points to be noticed are:

(1) Nitrogen is generally a gas; phosphorus, a vitreous solid; and vanadium, a semi-metal. The nitrogen compounds are easily decomposed; the phosphorus compounds are exceedingly pliant, changing readily from one form to another. These qualities fit them for the laboratory of nature, and we find them necessary both to vegetables and animals.

(2) The pentoxides of the second sub-group yield ortho-, pyro-, and meta- "ic" acids, which form "ate" salts that are isomorphous and generally agree in their properties.

(3) The elements of the third sub-group are either poisonous (P) or form poisonous compounds (As and Sb). Sb alone forms no ortho-, oxy-acid. The molecule of P and of As contains 4 atoms; that of Sb has not been determined.

(4) The oxides of the fourth sub-group form a decreasing series as regards their acid properties. Those of P are generally acid anhydrides; Sb_2O_3 is either acid or basic; Sb_2O_5, acid; Bi_2O_3, basic; and Bi_2O_5, feebly acid.

(5) The sulphides of the fifth sub-group are all sulpho-anhydrides, which form with sulphides of many metals sulpho-salts analogous to the oxy-salts.

The formula of the chloride of nitrogen is unknown. All the terchlorides of the remaining elements are decomposed by water, forming generally oxy-chlorides of the formula (RO) Cl. (See also § 212). Imagine in these compounds the chlorine to be removed; there will remain a monatomic radical of the formula $(R'''O'')'$, which is represented in $(SbO)'$, $(AsO)'$, and probably by $(BiO)'$ in basic bismuthous compounds.

CHAPTER VIII.

BORON.

Symbol, B. Atomic weight, 11. Specific gravity, 2.68.
Melts about 300° C. Isolated by Gay-Lussac in 1808.

277. Boron is a triad element which derives its chief importance from boracic or boric acid, H_2O, B_2O_3 or HBO_2.

Borax ($Na_2O, 2B_2O_3, 10H_2O$ or $Na_2B_4O_7, 10H_2O$) is found native as tincal in certain lakes of Asia and California. Boric acid is found native as sassolite. It is principally obtained from the volcanic districts of Tuscany.

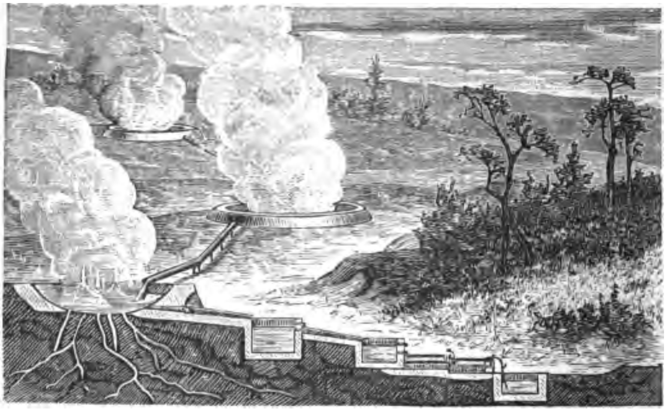

FIG. 75.

In that country numerous jets of steam, called *suffoni*, issue from fissures in the ground, and are condensed into natural or artificial ponds called lagunes. The water in these lagunes contains dilute boric acid; and, on evaporation, which is carried on by the natural heat of the suffoni, yield a crude boric acid. This is either purified by re-crystallization or is employed in the manufacture of borax. Pure boric acid may be obtained from borax.

Exp. 158.—Boil 3 parts of borax in 12 of water, and to the hot solution, filtered if necessary, add 1 part of strong sulphuric acid. On cooling, boric acid separates in white, pearly looking scales, unctuous to the touch. These are the orthoboric acid, $3H_2O, B_2O_3$. When heated, they are converted to pyroboric acid, $H_2B_2O_7$; then to metaboric acid, HBO_2; and finally to the anhydride B_2O_3, which fuses to a transparent glass.

278. Boric acid is soluble in 25 parts of water at 18° C., and in 3 parts at 100° C. It must be reckoned as a feeble acid: its solution colors litmus a dark wine red, and turmeric a brown red. At high temperatures, fused boric acid, and also borax, dissolves many metallic oxides to form transparent glassy borates. Hence they are employed as fluxes in soldering, and are often added to enamels to render them more fusible. Large quantities of borax are used in glazing stone-ware.

Exp. 159.—Bend the end of a thin platinum wire into a small loop. Heat this and touch it to a small fragment of dried borax. The borax will adhere to the wire. Now introduce the borax into the flame of a Bunsen's lamp. It will fuse to a clear glassy bead.

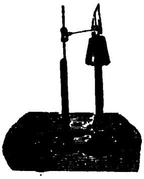

FIG. 76.

Very small quantities of several of the metallic oxides produce characteristic colors when they are added to the borax bead, and hence these beads are often used in blowpipe testing.

Exp. 160.—Just touch the borax bead with cobalt nitrate; then melt the bead again. It will become a beautiful blue. Manganese gives an amethyst bead in an oxidizing flame; chromium and copper, a green bead; ferric oxide gives a greenish yellow bead. Many oxides, like those of silver, nickel, and lead, yield grayish beads in the reducing flame, owing to the presence of the reduced metal.

279. Test. Boric acid is detected by its imparting a a green color to flames.

Exp. 161.—(I) Dissolve a little boric acid in alcohol, and ignite. A beautiful green flame is produced, which, when examined by the spectroscope, is resolved into a series of five green bands.

(II) Form a borax bead on a platinum wire; then moisten it with strong sulphuric acid. On bringing this into a colorless flame, the green flame characteristic of boron will be produced.

280. Boron may be obtained as an amorphous, brown powder by heating vitrified boric anhydride with sodium. It has also been obtained as graphitoidal boron in brilliant scales, like graphite, and as adamantine boron in brilliant, highly refracting crystals which resemble the diamond both in their luster and hardness. These latter are thought to be allotropic forms of boron; but the adamantine always contains carbon, and the graphitoidal, aluminum.

Its physical properties strongly resemble those of carbon and silicon, with which it was formerly classed. All form feeble acids by direct union with oxygen, whose salts also frequently resemble each other. Their relationship may be expressed graphically thus:

$$\begin{tikzcd} B'''11 \arrow[dr, dash] & & C^{IV}12 \arrow[dl, dash] \\ & Si^{IV}28 & \end{tikzcd}$$

Recapitulation.

Boron is the only triad in the list of the non-metals.
Its principal salt is borax.

CHAPTER IX.

THE CARBON GROUP.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	FUSING POINT. °C	DISCOVERER.
Carbon	C	12	3.33		
Silicon	Si	28	2.49		Berzelius, 1823.
Titanium	Ti	50	5.3?		Gregor, 1791.
Zirconium	Zr	89.6	4.15		Klaproth, 1789.
Tin	Sn	118	7.29	230°	

281. This is a group of tetrad elements. All of them unite with four atoms of chlorine to form tetrachlorides. Carbon and silicon form gaseous, inflammable compounds with four atoms of hydrogen, as CH_4; SiH_4. All of the elements in this group form dioxides and disulphides, which unite as acids with the alkaline oxides and sulphides to form oxy- and sulpho-salts, as K_2O, C_2O; K_2S, CS_2.

Carbon and tin also act as dyads in a few compounds; as CO, $SnCl_2$, SnO, SnS. These compounds are either indifferent bodies, or they possess feebly basic properties.

Carbon and silicon are non-metals whose physical properties resemble those of the triad element boron. One of their allotropic conditions, the graphitoidal, has some of the physical characters of the metals, viz, their luster and the property of conducting heat and electricity.

Zirconium, titanium, and tin are semi-metals very closely resembling each other, and are allied in their physical properties to the metals.

282. Carbon is remarkable for the great number of its hydrogen compounds. These are spoken of collectively as the *hydrocarbons*, and include the greater number of the essential oils, coal oils, and the gases used for illumination. They are generally classed together and studied in *organic chemistry*, which may be defined as the "chemistry of the carbon compounds." Only the oxides and sulphides will be presented in this chapter.

CARBON.

283. Carbon is one of the most abundant elements. In combination it is an essential constituent of all organic substances; of all carbonates, such as limestone, and is found in the air in carbonic anhydride. In the free state it occurs in three allotropic forms: (1) pure in the diamond; (2) nearly pure in graphite; and (3) less pure in anthracite coal. Carbonado, gas carbon, coke, lampblack, and charcoal are varieties of these. Bituminous coal, asphalt, and jet contain also hydrocarbons which are volatilizable by heat.

Physical Properties of Carbon.

284. (I) **The diamond occurs** as small, rounded bodies in the detritus of certain quartzose rocks which are found principally in Golconda, Brazil, and South Africa. Its crystalline form is that of the octahedron: sp. gr. 3.5. It has a brilliant luster, which is increased by cutting so as to furnish numerous facets capable of reflecting and refracting light in various directions. It is the hardest substance known, and hence can be cut only by means of dust obtained by pounding up the least valuable sorts of diamonds. When broken, the diamond naturally cleaves in directions nearly parallel to other faces of the octahedron, but generally in faces more or less curved. These curved faces intersect in curved edges, which are more suitable than straight edges for cutting glass, as they are capable of penetrating the glass like a wedge, instead of merely scratching its surface.

The *carbonado*, a black diamond found in Brazil, has lately been employed in rock cutting to great advantage.

285. (II) **Graphite** is occasionally found in six-sided plates which belong to the rhombohedral system. It generally occurs in the amorphous state, and is known as plumbago or black lead: sp. gr. 2.2. Graphite has a dark, steel-gray color, a semi-metallic luster, and is unctuous to the touch. It is found generally in the older rocks, and occurs most abundantly in Ceylon, Siberia, and California. The graphites of Cumberland, England, and of Ticonderoga, N. Y., are especially noted for their purity. Some varieties of cast iron contain so much graphite that it separates in the crystalline form (*kish*) when the molten iron is slowly cooled.

Graphite is used for making lead-pencils and crucibles, for polishing stoves, and as a lubricant to diminish the friction of machinery. It is a conductor of electricity, and is used in the electrotype process to impart a conducting surface to non-conducting materials, such as wax.

286. (III) **Mineral coal exists** in three principal varieties: anthracite, bituminous, and lignite. These are all undoubtedly of vegetable origin; and it is possible to form a series beginning with peat, in which much of the material is not thoroughly carbonized; through lignite, in which the woody structure is clearly apparent; cannel coal, from which large quantities of the so-called coal oils may be distilled; bituminous coal, which readily cakes together when heated, and burns with a bright blaze; non-caking bituminous coal; anthracite coal, which contains 90 per cent of carbon; to the coals of Greenland, which are sometimes regarded as graphite.

287. (IV) **Bituminous coals,** when distilled, yield a large number of volatile hydrocarbons, and a porous, often brilliant looking solid, which is known as *coke.* It is an accidental product in the manufacture of illuminating gas, but is also purposely prepared for iron smelting, to obtain a fuel that does not cake in burning.

Another very dense and hard form of carbon, which is slowly produced in gas retorts by the decomposition of the volatile hydrocarbons; is known as gas carbon. It is used as the negative element in many forms of galvanic batteries. The carbon plates are usually prepared by compressing a mixture of coke, coal, and treacle in iron moulds, and then strongly heating the mixture.

288. (V) **The imperfect combustion** of organic substances also yields various forms of carbon. Wood charcoal is generally made by piling billets of wood in large heaps, which are covered with turf,—holes being left at the bottom for the air to get in, and a flue left open at the middle of the heap. The heap is then kindled at the center, and, when the combustion is well established, the flue is closed and the mass is allowed to smoulder until the wood is perfectly carbonized. A better method consists in heating the wood in iron cylinders.

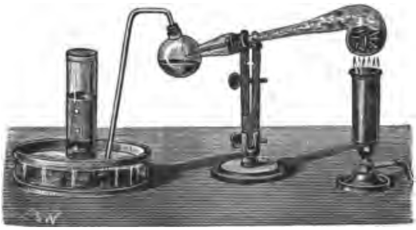

FIG. 77.

Exp. 162. — Place in a glass retort splinters of wood, and arrange the apparatus as shown in Fig. 77. On heating the retort, inflammable gases will collect in the cylinder over water; tar, water, methylic alcohol, and acetic acid, in the receiver; and charcoal will remain in the retort.

The charcoal remaining weighs about one-fourth of the original wood. It retains the general structure of the wood; even to the concentric rings. Owing to its porous nature, it is capable of absorbing large amounts of gases; it absorbs 90 times its volume of ammonia, and 55 times its volume of sulphuretted hydrogen. Hence it is of great use in purifying drinking water, and as a deodorizer for putrefying matters. Those gases are best absorbed that are easily condensed, seeming to indicate that the absorbed gases assume in part a liquid condition.

Exp. 163.—Fill a long glass tube with dry ammonia over a trough containing mercury, and then introduce a fragment of charcoal recently ignited and cooled under mercury. In a short time the coal will so absorb the ammonia that the mercury will be forced up the tube. (Use apparatus in Fig. 1).

289. (VI) **Animal charcoal** is made by heating crushed bones in iron retorts. It is a mixture of very finely divided coal and calcium phosphate. It is largely used for decolorizing sugar syrups and in refining alcohol.

Exp. 164.—To show these properties, shake a handful of freshly ignited animal charcoal with an infusion of logwood: boil, and then filter the mixture through paper. The liquid will have lost its color.

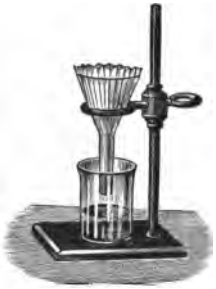
FIG. 78.

It is important to observe that in many cases other bodies than the coloring matters are retained by the charcoal. Thus, it removes the bitter principle of beer, and, what is more important, most of the alkaloids—as quinine and strychnine—from their solutions.

290. (VII) **Lampblack** is the soot obtained by the imperfect combustion of resinous, tarry, or oily matters, or of the natural gases of petroleum.

Exp. 165.—Set fire to a lump of resin, and hold a cold white plate over the flame. Abundance of soot will be deposited upon it.

If the first product is calcined in a covered crucible, a very nearly pure form of carbon is obtained. Its impurities, however, do not affect its employment as a pigment in the manufacture of paint, printing ink, and blacking.

All these forms of carbon are practically infusible, although it is stated that, at the exceedingly high temperature of the voltaic arc, phenomena have been observed which indicate its fusion and volatilization.

291. Chemical properties. At ordinary temperatures, all these forms of carbon are chemically inert. Manuscripts written with an ink made of lampblack, still perfectly legible, have been exhumed with Egyptian mummies. It is a common practice to char the ends of wooden stakes which are intended to be sunk in the ground, so that the interior may be protected from decay by a superficial coating of charcoal.

At high temperatures, carbon enters into direct combination with oxygen, sulphur, hydrogen, nitrogen, and a few of the metals. Porous wood charcoal ignites in the air at 240° C.; anthracite requires a much higher temperature; and the diamond, the highest temperature of all the forms of carbon. At very high temperatures, the affinity of carbon for oxygen is so great that it is capable of removing oxygen from its compounds with the metals. Hence, it is largely employed as a reducing agent by the metallurgist. (See Exp. 154).

Exp. 166.—Mix basic bismuthous nitrate with an equal bulk of charcoal in fine splinters, and heat this mixture in a crucible to ignition. (For apparatus, see Fig. 67). On cooling, a bead of metallic bismuth will be found in the crucible. A little decrepitated sodium chloride may be placed to advantage on the top of the crucible, so as to exclude the air.

Repeat this experiment with litharge.

Heated coal is even able to decompose water. Thus, if steam be passed over red-hot charcoal (use apparatus in Fig. 7), the carbon will unite with its oxygen, liberating hydrogen and forming carbonous oxide and carbonic anhydride:

$$4H_2O + 3C = \widehat{CO}_2 + 2\widehat{CO} + \widehat{H}_8.$$

292. The compounds of carbon and oxygen are carbonous oxide and carbonic anhydride. Both are aëriform bodies, formed by the direct union of the two elements when any form of carbon is burned in air. When the supply of air is abundant, nearly pure carbonic anhydride is produced; but when the supply is limited, it is mixed with carbonous oxide.

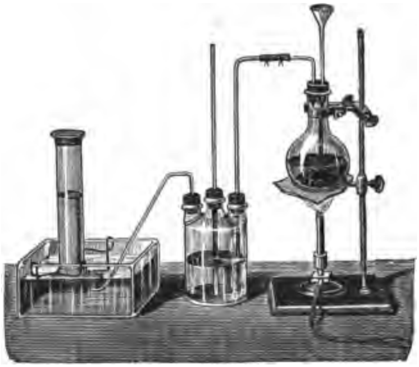

FIG. 79.

293. Carbonous oxide, CO, is more frequently known by the name of carbonic oxide. It may be prepared by gently heating thoroughly dried potassium ferrocyanide with four times its weight of sulphuric acid, and washing the gas with a solution of potassium hydrate. (Fig. 79). The lamp must be removed as soon as the gas begins to form rapidly.

$$K_4Fe(CN)_6 + 6H_2O + 6(H_2SO_4) = 6\widehat{CO} + 2(K_2SO_4) + FeSO_4 + 3[(H_4N)_2SO_4].$$

It is also produced by the reaction mentioned in § **292**.

294. Physical properties. Carbonous oxide is a permanent, colorless gas, nearly insoluble in water: sp. gr. 0.967. It is completely absorbed by a solution of cuprous chloride.

295. Chemical properties. Carbonous oxide burns in the air with a pale blue flame and forms carbonic anhydride, CO_2. Conversely, carbonic anhydride is readily reduced to carbonous oxide. Thus, when the air enters at the bottom of a clear fire, the oxygen at once unites with the carbon to form carbonic anhydride. As this gas passes through the heated embers above, it is reduced by the coals to carbonous oxide ($CO_2 + C = 2CO$). The blue flame which is noticed on the top of anthracite fires is produced by the combustion of this carbonous oxide in the fresh air above the coals.

Carbonous oxide is a reducing agent. It may be employed instead of hydrogen to reduce cupric or ferric oxide in the apparatus shown in Figs. 7 or 27.

The reactions already mentioned play an important part in many metallurgical operations.

Thus, in the reverberatory furnace represented in Fig. 80, the metallic oxides are placed on the hearth and the fuel at the side. The fuel is burned so as to yield carbonous oxide, which then plays over the hearth, abstracts the oxygen from the ores, and reduces them to the metallic state. The production of this oxide is increased by placing pans of water below the bars, so that steam may be formed and produce the reaction mentioned in § 292.

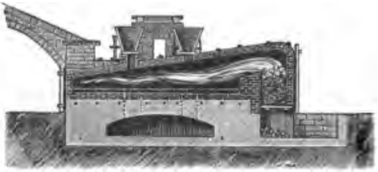

FIG. 80.

Carbonous oxide unites directly with chlorine, sulphur, and potassium, but it does not form salts with either acids or bases. It is regarded as the free state of the diatomic radical carbonyl, and enters as such into many organic compounds.

296. When carbonous oxide is passed over hot, moistened potassium hydrate, potassium formiate is produced: $KHO + CO = KHO, CO$; or KO, CHO; or $K, COOH$.

This is an interesting reaction, as from this salt formic acid, HO, CHO, may be prepared, an example of the *synthesis* of organic bodies from inorganic materials.

297. Physiological properties. Carbonous oxide is so poisonous that one per cent of it diffused through the air produces giddiness in those that breathe it, and, after a while, a fatal result through suffocation.

298. Carbonic anhydride, CO_2. We have already noticed that this body is produced by the complete combustion of carbon and of carbonous oxide. It is also produced by the processes of respiration, fermentation, and decay. As these processes are going on continually, enormous quantities of carbonic anhydride would accumulate in the air, were it not that the leaves of plants, under the influence of sunlight, decompose this gas, assimilating the carbon to form woody tissue and other vegetable products, and giving back the oxygen to the air. This so maintains the balance of nature that the average quantity of carbonic anhydride in the atmosphere is about one twenty-five hundredth part of the whole. Liquors like champagne and soda water owe their effervescing character to the carbonic acid which has been retained in them by pressure.

299. Preparation. Carbonic anhydride is usually prepared by the action of dilute acids upon the carbonates.

Exp. 167.—Place a few fragments of marble in a flask, and pour upon them dilute hydrochloric acid. The gas may be collected over water or by displacement. (Use apparatus in Fig. 20).

$$CaO, CO_2 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

300. Physical properties. Carbonic anhydride is a colorless, coercible gas, having a peculiar, pungent odor. Its specific gravity (1.529) is so great that it may be poured from one vessel to another (Fig. 81); and, consequently, its rate of diffusion is so small that it sometimes accumulates in wells and caverns. This is notably seen in the *Grotto del Cane*, near Naples.

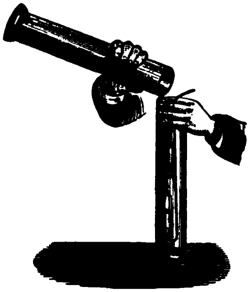

FIG. 81.

At ordinary temperatures, carbonic anhydride is condensed by a pressure of 50 atmospheres to a colorless liquid: sp. gr. 0.83. If this liquid anhydride is liberated from pressure, a portion rapidly volatilizes, and, by so doing, produces a cold of —77° C., which is sufficient to freeze the remaining portion into a snow-white, flocculent mass. This may be handled notwithstanding its low temperature, because it is kept from contact with the hand by a layer of the gas (spheroidal condition); but, if pressed into actual contact with the skin, it produces a blister like a burn. Wetted with ether, it easily solidifies mercury, and *in vacuo* produces a cold of —110° C.

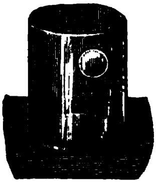

FIG. 82.

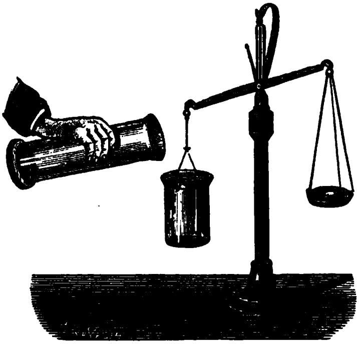

FIG. 83.

301. Chemical properties. Carbonic anhydride is incombustible, and extinguishes the flame of ordinary combustibles. Its high specific gravity and power of extinguishing flame may be illustrated by the following experiments.

Exp. 168.—An ordinary soap bubble will float on the surface of the gas. Evolve the gas in a broad-mouthed jar by placing marble chippings and acid at the bottom. (Fig. 82).

Exp. 169.—Balance a light paper box on an arm of a balance: the anhydride may be poured into the box and will depress the beam. (Fig. 83).

Exp. 170.—A lighted taper plunged into the gas will be extinguished. It may also be extinguished by pouring the gas upon it from some distance above. (Fig. 81).

Exp. 171.—The gas may be drawn up in buckets from the bottom of large jars and used as in Exps. 169 and 170. It may be reduced to carbonous oxide by ignited coals, and also by some metals, as Zn and Fe, at high temperatures.

Exp. 172.—Pass a dry stream of the gas over melted sodium. It is in part reduced to carbon, while another part combines with the sodium. (Fig, 82). $3CO_2 + Na_4 = 2(Na_2O, CO_2) + C$. The product formed in this case is the normal sodium carbonate, Na_2CO_2.

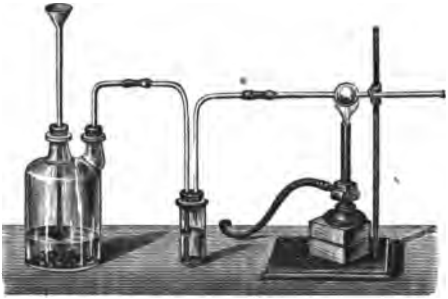

FIG. 84.

Potassium hydrate rapidly absorbs the gas, and may be used to separate it from mixtures with most other gases. When a large excess of the gas is passed into a solution of potassium hydrate, the product formed is $KHCO_3$, acid potassium carbonate, or bicarbonate of potassa. Similar salts are formed with the other metals. There are also sesquicarbonates which may be regarded as mixtures of the other two, as $2NaHCO_3 + Na_2CO_3 = Na_4H_2, 3CO_3$, and orthocarbonates like half-burned lime, $2CaO, CO_2$ or $Ca''_2 CO_4$.

The solution of the gas in water (§ **36**) is regarded as *carbonic acid*, but it has not been isolated. Its theoretical formula should be $C^{IV}(OH)_4$ or H_4CO_4, a tetrabasic ortho-acid. Generally speaking, it acts as a dibasic acid, having the formula H_2CO_3 or H_2O, CO_2.

Carbonic acid is a feeble acid that is easily displaced by almost all other acids. All the carbonates, except those of the alkalies, are decomposed by heat. These are decomposed when boiled with calcium hydrate.

302. Physiological properties. Carbonic acid is not poisonous when taken into the stomach, but the gas acts injuriously when breathed, except when exceedingly dilute. Fatal accidents have occurred from the accumulation of this gas in old cisterns, brewers' vats, and in mines, where it is known by the name of "choke damp." Air containing one per cent of carbonic anhydride produces in most persons languor and headache; a larger proportion causes stupor; and nine per cent is sufficient to cause suffocation and death.

The air expired from the lungs contains about four per cent of the gas. Air which has been twice respired contains enough of the gas to extinguish a taper. A full-sized man evolves from his lungs and skin about 0.7 cubic foot per hour of carbonic anhydride. In order that he may continue to breathe without inconvenience, it is necessary that this evolved gas should be distributed through at least 140 cubic feet of fresh air, so that it may not exceed one-half of one per cent of the air. Hence, there is a necessity for abundant ventilation of occupied apartments. It should be remembered that lamps also produce carbonic acid. A gas burner consuming six feet of gas per hour evolves as much carbonic acid as one man.

303. Uses. Carbonic anhydride has proved of great service in extinguishing fires in coal mines; and several devices have been proposed by which it may be turned to account in extinguishing ordinary conflagrations. Water containing carbonic acid is of great importance in the chemistry of Nature. It is capable of dissolving calcium carbonate and other bodies not soluble in pure water, and thus assists in disintegrating rocks and preparing soils for the uses of plants. The gas is also used in manufacturing various carbonates, as those of sodium and lead.

304. Tests. Free carbonic anhydride may be recognized by passing it into lime-water (Fig. 5), when it causes a precipitate of calcium carbonate.

Exp. 173.—The presence of this gas in expired air may readily be shown by blowing a deep breath into lime-water. (Fig. 85).

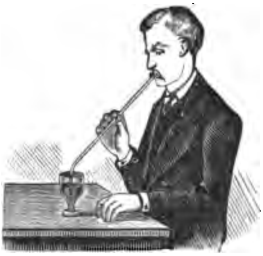

FIG. 85.

Exp. 174.—The carbonic anhydride in air may be shown by the following apparatus. A wide tube, a foot long, is placed in an inclined position, and is fitted at both ends with vertical tubes. It is then half-filled with lime-water. The air slowly drawn through this by means of an aspirator renders the lime-water milky. The aspirator may consist of a large can furnished with a siphon, as shown in Fig. 86.

The carbonates are known by their effervescing and by evolving CO_2 when a strong acid is poured upon them.

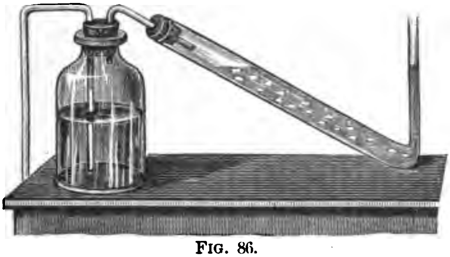

FIG. 86.

305. Carbonic disulphide, CS_2, is prepared by passing the vapor of sulphur over coke or charcoal heated to redness. It is frequently present as one of the most injurious impurities in coal gas.

306. Physical properties. Carbonic disulphide is a colorless, diathermanous liquid of high refracting powers (1.645), and, when pure, of not unpleasant odor: sp. gr. 1.27. Usually, however, the odor of its vapor is very offensive. It volatilizes rapidly at ordinary temperatures, producing great cold, and boils at 46.6° C.

Exp. 175.—Place a watch glass filled with carbonic disulphide on a glass plate covered with water, and evaporate it rapidly by blowing a current of air over its surface. The glass will be frozen to the plate.

It has never been solidified by cold. Its vapor is so inflammable that it may be ignited by a glass rod heated below redness (Fig. 87); consequently, great care should be used in experimenting with it.

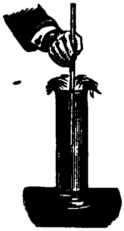

FIG. 87.

307. Chemical properties. Carbonic disulphide is a sulphur acid, capable of combining with alkaline sulphides to form sulphocarbonates, as K_2S, CS_2. It is easily decomposed into its elements, carbon and sulphur, and hence may be used to form various carbon and sulphur compounds.

308. Uses. Carbonic disulphide is an excellent solvent for phosphorus, iodine, sulphur, many resins, and oils. It is very extensively used in the extraction of fats and oils, and in the cold process of vulcanizing caoutchouc. The poisonous properties of its vapor have been turned to account for killing insects in grain.

SILICON OR SILICIUM.

309. Silicon is always found in combination with oxygen, either alone as silicic anhydride (SiO_2), in the form of quartz or sand, or united with various metallic oxides, forming silicates.

310. Preparation. Silicon is prepared by heating dry potassium silico-fluoride with potassium or aluminium.

$$2KF, SiF_4 + K_4 = 6KF + Si.$$

311. Physical properties. Silicon may be obtained in three forms: (1) a soft, brown, amorphous powder; (2) as hexagonal plates, which resemble graphite in luster and power of conducting electricity—sp. gr. 2.5; and (3) in iron-gray needles or octahedra, which are so hard as to scratch glass like the diamond. All these forms are fusible at a temperature between 1600° C. and 1800° C.

312. Chemical properties. Amorphous silicon burns brilliantly in air to SiO_2, and dissolves in hydrofluoric acid to SiF_4. The other forms of silicon are incombustible in air, and are insoluble in hydrofluoric acid.

Like carbon, silicon is found in cast iron and in certain other metals, either mixed or in compounds which resemble alloys; but, unlike carbon, it forms but one known compound with hydrogen, and that of a very unstable character. It must, however, be remarked that numerous alcohols and ethers are known which contain silicon in place of carbon.

313. Hydrogen silicide, H_4Si, is prepared by decomposing magnesium silicide by dilute hydrochloric acid. $Mg_2Si + 4HCl = H_4Si + 2MgCl_2$. It is a colorless gas, insoluble in water that is free from air.

314. Chemical properties. Pure hydrogen silicide is not spontaneously inflammable at ordinary temperatures, but is easily decomposed by heat into amorphous silicon and hydrogen. When mixed with hydrogen, it ignites in the air spontaneously, evolving silicic anhydride, and depositing on a cold surface a brown film of silicon.

315. Silicic anhydride, or silica, SiO_2. The purest natural variety of silica is quartz, or rock crystal. This is found in beautiful, six-sided prisms, terminated by six-sided pyramids. It also occurs crystalline very nearly pure—as amethyst, rose quartz, and Cairngorm stones; and in the amorphous form—as jasper, agate, onyx, carnelian, chalcedony, and flint. The opal is silica combined with water. The whiter varieties of sand are nearly pure silica; the yellow color of ordinary sand and sandstones is due to the presence of an oxide of iron.

316. Preparation. The gelatinous precipitate which forms when silicon fluoride is decomposed by water, is a compound of silicic anhydride and water, which may be regarded as silicic acid. If this is washed and dried, the white powder which is left is silicic anhydride.

317. Physical properties. Quartz is so hard as to be able to scratch glass: sp. gr. 2.5 to 2.9. The artificial silica is so finely divided that it is remarkable for its extreme mobility, the slightest breath easily blowing it away. All varieties of silica are infusible except by the extreme heat of the oxy-hydrogen flame.

318. Chemical properties. Ignited silicic anhydride is insoluble in all acids except hydrofluoric. It unites with the alkalies, either on boiling with their solutions or on fusing in the dry state, forming silicates which are soluble in water. These compounds are known as soluble glass.

319. Silicic acid. If a solution of an alkaline silicate be slightly acidulated with hydrochloric acid, the gelatinous precipitate which forms is probably $2H_2O, SiO_2 = H_4SiO_4$, or orthosilicic acid. In this state it is readily soluble either in alkalies or in hydrochloric acid. Silicic acid soluble in water may also be obtained by dialysis.

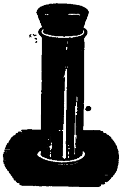

FIG. 88.

Exp. 176.—Support a cone of parchment paper in a vessel filled with distilled water, so that the water may come in contact with the outer surface of the cone, and fill the cone with a solution of silica in hydrochloric acid. In a few days the alkaline chlorides derived from the soluble glass and the hydrochloric acid will dialyze through the paper, and a solution of silicic acid in water remain in the cone.

This solution may be evaporated *in vacuo* to a transparent glass, which is metasilicic acid, $H_2O, SiO_2 = H_2SiO_3$. The solution has a great tendency to assume the gelatinous form, and can not be preserved.

Many thermal springs also contain silica in solution. The Geysers of Iceland contain considerable quantities, and, as the liquid cools, deposit the silica upon objects exposed in their basins. In these cases we must suppose the solvent power to be due to the presence of alkaline carbonates, assisted by the high temperature. Silica dissolved in soil is taken up by plants; notably so by the cereals, grapes, and rushes. It forms beautiful crystals in the leaves of the *Deutzia scabra.*

320. The natural silicates are very numerous, and are often of a very complex nature. Among these are clay and kaolin ($Al_2O_3, 2SiO_2$), potash mica ($Al_6K_2O_{10}, 6SiO_2$), common mica ($Mg_4Al_2O_7, 2SiO_2$), garnet ($Ca_3Al_2O_6, 3SiO_2$), the feldspars, orthoclase ($K_2Al_2O_4, 6SiO_2$), and albite ($Na_2Al_2O_4, 6SiO_2$). Talc, meerschaum, serpentine, and hornblende are principally silicates of magnesia.

321. Of the artificial silicates, only those of the alkalies are soluble in water. These are largely used, under the name of soluble glass: (1) in mural paintings; (2) for the preservation of building stone; (3) for cleansing wools; and (4) in preparing mordanted calicoes for dyeing.

Glass is a mixture of an alkaline silicate with one or more insoluble silicates. Glass is made by fusing silica with potash or soda and some base which is calculated to render the mixture less soluble, more infusible, or more transparent. Crown glass is a silicate of potash and lime; flint glass is a silicate of potash and lead:

ordinary window glass is a silicate of soda and lime. The cheaper forms of glass generally contain also silicates of alumina and of iron. Ferrous oxide imparts a green color to glass, but ferric oxide gives only a yellowish tinge. Hence, the green color due to iron may be prevented by the addition of some oxidizing agent, as arsenious acid or niter. Manganese dioxide imparts a purple color to glass. If green and purple glasses are fused together, a colorless glass results. We may suppose this effect to be produced either by reason that the two colors are complementary to each other, or that the manganese acts as an oxidizing agent. Colored glass is produced by small quantities of various substances:—red, by cuprous oxide; ruby, by gold; yellow, by antimony; blue, by cobalt; white enamel, by stannic oxide. The glass used for imitation of precious stones contains generally a large proportion of lead oxide, also frequently baryta and boracic acid.

TESTS.—Silica may be recognized, (1) by its insolubility in acids; (2) by its infusibility before the blowpipe. (3) Make a bead of microcosmic salt ($NaNH_4HPO_4$) on a loop of platinum wire, and add a trace of a silicate. On again fusing the bead, the silica will remain undissolved and will float as a spongy mass (silica skeleton) in the molten bead. An excess of silica renders the bead opaque.

TIN.

322. The only important ore of tin is cassiterite, or tin stone, SnO_2. This is found mixed with other metallic ores in veins traversing the primitive rocks, and also, in a purer condition, as stream tin ore, in the alluvial deposits which are formed by the natural disintegration of these rocks. The largest supplies of tin are obtained from Cornwall, Malacca, Banca, and Australia.

323. Preparation. Tin is obtained by smelting the ore mixed with pulverized anthracite or charcoal.

324. Physical properties. Tin is a soft, white metal: sp. gr. 7.29. It fuses at 228° C., but is not easily volatilized. Its tenacity and ductility are very low, but it is highly malleable, as is shown in the manufacture of tin foil. It exhibits a considerable tendency to crystallize. A bar of tin, when bent, emits a peculiar, creaking sound, which is probably due to the interior crystals breaking against each other.

Exp. 177.—Wash the surface of tin plate with warm, dilute nitro-hydrochloric acid. In a little while, a mass of crystalline forms will appear (*moirée metallique*).

325. Chemical properties. Tin unites readily with sulphur, chlorine, phosphorus, and oxygen, when heated with these elements. It retains its luster for a long time, even in the presence of moist air; but, when fused in air, rapidly oxidizes to white stannic oxide, SnO_2. It forms two series of compounds: the stannous, in which it is bivalent, and the stannic, in which it is quadrivalent.

326. Uses. Tin is generally employed in alloys and as a coating for other metals. Tin plate is simply a sheet of iron covered with tin. It is made by carefully cleansing iron plates from every trace of oxide, and then immersing them in melted tin. A cheaper variety, terne plate, is coated with an alloy of tin and lead. Brass pins are coated with tin by boiling them in water containing granulated tin, acid potassium tartrate, alum, and common salt.

Among the alloys of tin are solder and pewter ($Sn + Pb$), Britannia metal ($Sn + Cu + Sb$), gun metal, bronze, and bell metal ($Cu + Sn$). The silvering applied to the backs of mirrors is tin foil amalgamated with mercury.

327. Stannous chloride, $SnCl_2, 2H_2O$, is obtained in prismatic needles by dissolving tin in hydrochloric acid.

It has a strong attraction both for chlorine and oxygen. and hence acts as a powerful reducing agent.

Exp. 178.—Add to a solution of $HgCl_2$ a drop or two of $SnCl_2$: calomel will be formed. $2HgCl_2 + SnCl_2 = \underset{\downarrow}{Hg_2}Cl_2 + SnCl_4$. Now add the $SnCl_2$ in excess: the precipitate is dark gray, metallic mercury. $Hg_2Cl_2 + SnCl_2 = 2\underset{\downarrow}{Hg} + SnCl_4$.

Stannous chloride is converted by water into an insoluble oxychloride (Sn_2Cl_2O). This change may be prevented by the addition of either hydrochloric or tartaric acid. It is used by the dyer as a deoxidizing agent, under the name of "tin salt."

328. Stannic chloride, $SnCl_4$, may be obtained as a heavy, fuming liquid by heating tin filings in dry chlorine gas. It readily combines with a small quantity of water to form $SnCl_4, 5H_2O$; but an excess of water decomposes it. A solution of this chloride is readily prepared by dissolving tin in hydrochloric acid, to which a very little nitric acid has been added.

Stannic chloride forms double salts with the chlorides of the alkalies. The "pink salt," used by dyers in the production of red colors, is $2NH_4Cl, SnCl_4$.

329. Stannous oxide is formed as a white hydrate, $2SnO, H_2O$, by precipitating stannous chloride with sodium carbonate. On boiling this mixture, the anhydrous oxide, SnO, forms as a brown powder.

It is a weak base which dissolves in acids to form stannous salts. The moist hydrate readily absorbs oxygen and becomes stannic oxide. Caustic potash converts it into metallic tin and stannic oxide, which combines with the potash.

330. Stannic oxide, SnO_2, is formed when tin is fused in contact with the air, or when either of the hydrates are strongly ignited. It is a white powder so hard that it is used for polishing, under the name of "putty powder." It is insoluble in acids, but, when fused with the alkalies, forms soluble compounds which are called stannates.

Sodium stannate, $Na_2O, SnO_2 = Na_2SnO_3$, is used as a mordant by calico printers. If a solution of this salt in water be acidulated with hydrochloric acid, a white, gelatinous precipitate falls; this is H_2O, SnO_2. As it readily combines with metallic oxides, it is stannic acid; but it also dissolves in the stronger acids, and forms with them stannic salts, in which it plays the role of a weak base.

Metastannic acid, $5H_2O, 5SnO_2 = Sn_5H_{10}O_{15}$, is formed by the action of nitric acid upon metallic tin. It is entirely insoluble in acids, but forms soluble metastannates with the alkalies.

331. Stannous sulphide, SnS, precipitates as a brown hydrate when hydrogen sulphide is passed into a solution of a stannous salt. When treated with the alkaline persulphides, it becomes SnS_2.

This stannic sulphide is also produced as a dull yellow hydrate when hydrogen sulphide is passed into solutions of stannic salts. It is sulphostannic acid, and dissolves easily in alkaline sulphides.

Stannic sulphide may also be produced in the dry way by carefully heating tin amalgam with sulphur and sal-ammoniac in a Florence flask. Beautiful yellow scales are left in the flask, which are called *mosaic gold*, and are used for decorative purposes.

332. Tests. The reactions mentioned in speaking of the preparation of the hydrated oxides and sulphides are tests for the salts of tin. Stannous chloride is distinguished from stannic chloride by its reducing action on mercuric chloride; and by its giving, with an excess of auric chloride, a precipitate, "the purple of Cassius" ($AuSnO_2$?). All tin compounds, when heated on charcoal with sodium carbonate, yield a malleable globule of tin.

333. Titanium and zirconium are rare tetrad elements. Titanium occurs in nature as titanic anhydride, TiO_2 (Rutile), but more frequently in iron ores as a titanate of iron. The slags obtained in smelting such ores with charcoal frequently contain copper-colored crystals which have the probable formula $Ti(CN)_2 3Ti_3N_2$. These are interesting, because they show the direct union of atmospheric nitrogen with titanium and carbon. When titanic anhydride is strongly heated in ammonia, it also forms TiN_2 (titanium nitride).

Zirconium has three allotropic states resembling those of silicium. Its principal oxide, ZrO_2 (zirconia), acts both as a base and as an acid. The sulphates of zirconium and of titanium are decomposed by a large excess of water.

Recapitulation.

These elements are grouped together because they act as tetrads, forming tetrachlorides (RCl_4) and acid anhydrides (RO_2), which form soluble salts with the fixed alkalies.

They may be divided into two sub-groups:

(*a*) Carbon, silicon.
(*b*) Titanium, zirconium, tin.

Carbon and silicon are non-metals which are remarkable for not conforming to the law of the specific heat of atoms (p. 55). Their compounds are very numerous and are of similar constitution.

The second sub-group consists of semi-metals, tin being popularly classed as a metal on account of its physical properties. Their compounds strongly resemble those of silicon.

Several of these elements form dyad compounds; as, CO, $SnCl_2$.

CHAPTER X.

THE ELECTRO-POSITIVE ELEMENTS.

334. The metals are distinguished from the elements previously studied principally in the fact that their oxygen compounds are generally basic. The semi-metals closely agree with them in their physical properties; and for this reason arsenic, antimony, bismuth, and tin will, in this chapter, be again grouped with the metals. They form undoubted alloys with the metals, and, as already stated, are a connecting link between the non-metals and the metals.

Physical Properties of Metals.

335. (I) **Great opacity.** Some metals, when in very thin sheets, are translucent. Thus, gold leaf transmits light of a green color.

336. (II) **Luster.** When the metals are very finely divided, as iron reduced by hydrogen (Exp. 30), they are generally dull looking powders; but when they are melted or beaten into a compact mass, they have in a high degree the power of reflecting light, which gives them the so-called metallic luster.

Exp. 179.—Add ferrous sulphate to gold chloride. Brown, metallic gold precipitates. On rubbing this, when dry, with a hard, smooth substance, it assumes the yellow luster of gold.

The natural luster of silver and of gold is very great. Metals which are hard enough to be polished, like iron in the form of steel, give splendid reflecting surfaces.

The mirrors or specula of the ancients were made of metals. An alloy of tin and copper is still used for this purpose in reflecting telescopes.

337. (III) **The color** of most of the metals is white or gray. Silver, tin, and sodium are almost pure white; iron, somewhat gray; lead and zinc, bluish; calcium, pale yellow; gold, full yellow; bismuth, reddish; and copper, a full red.

338. (IV) **A few metals yield a peculiar odor** when rubbed, as is the case with copper and tin. Many of their salts have an acrid *taste* which is called metallic. To the formation of these salts is due the peculiar taste observed when a tarnished piece of copper or brass is placed on the tongue.

339. (V) **Crystallization.** Many metals may be crystallized in some form of the isometric system, as the cube, octahedron, etc. The metals most easily crystallized are generally the brittle metals, as bismuth and antimony.

Exp. 180.—Melt several pounds of lead in a crucible and set it aside to cool. As soon as a crust has formed on the top, pour out the still molten interior, and a mass of interlaced octahedra will remain.

Exp. 181.—Suspend a bright strip of zinc in a dilute solution of lead acetate. After a few days, arborescent crystals of lead will be formed (*arbor Saturni*).

Some metals while in the solid state tend to assume a crystalline structure under the influence of repeated blows. The sudden breaking down of iron bridges and of iron axles in railway cars has been attributed to this cause.

340. (VI) **The cohesion of metals** varies greatly. At ordinary temperatures, mercury is a liquid; all the others are solids. Some of these, as sodium and potassium, are so soft that they may be kneaded like wax; others, as chromium and manganese, rival the diamond in hardness.

The soft metals and the brittle metals have generally little tenacity: lead and zinc are examples. A bar of steel one square inch in section has resisted a stretching force of nearly 180,000 pounds. Copper wire has about one-third of this tenacity.

341. (VII) **Many metals are malleable**; that is, they are capable of being flattened out under the hammer or between rollers; and are also *ductile*, or capable of being drawn into fine wires. The following table, which gives the relative tenacity, ductility, and malleability, shows that the metals do not possess these properties in equal degrees.

RANK.	TENACITY.	DUCTILITY.	MALLEABILITY UNDER THE HAMMER.	MALLEABILITY BETWEEN ROLLERS.
1	Iron	Platinum	Lead	Gold
2	Copper	Silver	Tin	Silver
3	Platinum	Iron	Gold	Copper
4	Silver	Copper	Zinc	Tin
5	Zinc	Gold	Silver	Lead
6	Gold	Zinc	Copper	Zinc
7	Lead	Tin	Platinum	Platinum
8	Tin	Lead	Iron	Iron

The ductility and malleability are increased, within certain limits, by a high temperature. Iron is rolled when at a white heat; zinc is most malleable when between 105° C. and 150° C.

342. (VIII) **All the metals are fusible.** Mercury, cadmium, zinc, magnesium, potassium, sodium, and rubidium are so readily vaporized that they may be purified by distillation. Others of the metals have been volatilized, but only at high temperatures.

343. (IX) **The specific gravity** of these elements exhibits a wonderful difference. Some are lighter than water. The common metals are from seven to nine times heavier than water (lead, 11.33). The *noble metals* are the heaviest bodies known.

The following table exhibits the specific gravities and fusing points of the metals.*

ELEMENT.	SPECIFIC GRAVITY.	FUSING POINT.
Lithium	.59	180° C.
Potassium	.86	62°.5
Sodium	.97	95°.6
Rubidium	1.52	38°.5
Calcium	1.58	
Magnesium	1.74	433°
Glucinum	2.10	1000°?
Strontium	2.54	
Aluminium	2.56	700°?
Barium	4.	450°
Arsenic	5.63	
Antimony	6.72	450°
Chromium	7.01	1900°?
Zinc	7.13	433°
Indium	7.42	176°
Tin	7.30	228°
Iron	7.84	1800°
Manganese	8.02	1800°?
Cadmium	8.56	320°
Molybdenum	8.63	1900°? C.
Nickel	8.82	1800°?
Copper	8.94	1200°
Cobalt	8.51	1800°?
Bismuth	9.8	270°
Silver	10.57	1023°
Lead	11.33	332°
Ruthenium	11.4	2000°?
Palladium	11.8	1900°?
Thallium	11.9	290°
Rhodium	12.1	2000°?
Mercury	13.6	—39°.4
Tungsten	18.3	1900°?
Uranium	18.4	
Gold	19.26	1250°
Iridium	21.15	2000°?
Osmium	21.4	2000°?
Platinum	21.5	2000°

344. Natural history. Few of the metals are found native. Among these are bismuth, gold, and platinum, which are almost always found in the state of metals; silver, mercury, and copper, which are found native less frequently; arsenic and antimony, which are seldom found uncombined with the other elements.

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* Temperatures above 1000° given in this table are only approximate.

Generally the metals occur as constituents of various minerals and ores. Lead, mercury, copper, zinc, and iron are frequently found united with sulphur. These sulphides often exhibit a brilliant luster, but have neither the ductility nor the tenacity of the metals. Tin, iron, and manganese are generally found as oxides. Calcium and sodium are sometimes met with as fluorides; and there are also chlorides of sodium and of potassium in enormous quantities.

Most of the minerals which constitute the solid crust of the globe are compounds of silica, alumina, lime, and magnesia. Thus, ordinary clay is mainly aluminium silicate; limestone is calcium carbonate; gypsum is calcium sulphate; the micas and feldspars are compounds of silica and alumina with other silicates of soda, potash, or lime; talc and serpentine are compounds of silica and magnesia. On the other hand, most of the ores which yield the metals that are useful in the arts seldom occur in large masses, but are collected in comparatively thin beds, or seams, called mineral veins.

345. Chemical properties. The metals exhibit strong affinities for the non-metals, and easily form stable compounds with them. Such, for example, are the binary compounds with oxygen, sulphur, and chlorine; as, Fe_2O_3, FeS_2, $NaCl$.

More commonly, ternary compounds are formed; as, for example, the hydrates of the alkalies, KHO, $NaHO$. The oxygen compounds, whether anhydrides or hydrates, are very generally basic. The protoxides are, almost without exception, strong bases; the strongest bases being those of the more electro-positive elements, as K, Na. The sesquioxides are generally weak bases, and in some cases may act as acids.

For example, Al_2O_3, aluminium sesquioxide, easily dissolves in sulphuric acid to form aluminic sulphate, $Al_2O_3, 3SO_3$, in which it plays the part of a base. It also dissolves easily in a solution of potassium hydrate to form K_2O, Al_2O_3, potassium aluminate, in which it plays the part of an acid.

The higher oxides of the metals are sometimes indifferent bodies, as MnO_2, PbO_2; or, when their highest stage of oxidation is reached, acid anhydrides, such as CrO_3, MnO_3, Mn_2O_7.

346. If a metal or its oxide is dissolved in an acid, a *salt* is formed. The acid loses the whole or a part of its hydrogen, which is replaced by the metal.

The halogen compounds of the metals, as $NaCl$, $CuCl_2$, are for the most part stable salts, not decomposed by water.

The ternary salts commonly contain a metal and a non-metal, or an acid radical, united by oxygen. Practically speaking, it makes but little difference what formula is assigned to these salts, if it correctly represents the percentage composition. The tendency among chemists is to use only the molecular formulæ.

347. Almost every metal has a long series of salts, as the carbonates, sulphates, nitrates, phosphates, etc. Not unfrequently each element has, besides the normal salt, others which are either basic or acid salts.

Besides these, we have a very interesting class of double salts. These very generally contain one kind of acid, but two or more bases, as $K_2Mg, 2SO_4 + 6H_2O$, and $KAl, 2SO_4 + 12H_2O$. A complete description of all these compounds would require many volumes of this size; hence, we shall attempt to give only the most important.

348. The metals, when melted together, form alloys. Such are brass (Cu and Zn), bell metal, and bronze (Cu and Sn). These alloys seem sometimes to be true chemical compounds; but, for the most part, are to be regarded as solidified mixtures containing, perhaps, a true compound with an excess of one of the ingredients.

The alloys of mercury with the other metals are called *amalgams.* The metallic surface of ordinary mirrors is an amalgam of mercury and tin.

349. Classification. The table on the following page, prepared by Mendelejeff, exhibits a very ingenious classification of all the elements. They are arranged in lines in accordance with their atomic weights:* the series, from left to right; the groups, from top to bottom. By this arrangement, elements which are similar in properties are brought in close juxtaposition; and thus those that show a marked gradation of properties are collected in natural groups. Some of these groups have been long recognized, as the chlorine group (7), the nitrogen group (5), the carbon group (4), which we have already studied. There are also natural groups among the metals, not less marked. Among these are the alkali group (1), the alkaline earths (2), the earths (3), which have so many points of resemblance that we might profitably consider each group as a whole before proceeding to the elements which compose it. Nevertheless, the grouping used in this book has been made rather for the convenience of the student than for the sake of any theory, however interesting and ingenious.

Recapitulation.

The metals differ from the non-metals in their physical properties; such as, opacity, luster, color, crystalline form, cohesion, tenacity, malleability, fusibility, specific gravity, etc. They also differ in their chemical properties, their lower compounds with O and S being generally basic. Some are found native, but generally as ores, containing O, S, and Cl; or as salts, containing CO_2 and SiO_2.

The compounds of the metals with each other are called alloys or amalgams.

All the elements may be so grouped as to show a natural gradation of properties.

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* Mendelejeff's atomic weights are frequently different from those on pp. 12 and 13, 59, and 60.

THE ELEMENTS.

SERIES.	GROUP 1.		GROUP 2.		GROUP 3.		GROUP 4.		GROUP 5.		GROUP 6.		GROUP 7.		GROUP 8.			
	$RCl-R_2O$		RCl_2-RO		RCl_4-RO_2		RCl_6-RO_3 H_4R		$RCl_5-R_2O_5$ H_3R		$RCl_6-R_2O_6$ H_2R		$RCl_7-R_2O_7$ HR		RO, R_2O_3, RO_2, R_2O			
I	H 1																	
II		Li 7		G 9.4		B 11		C 12		N 14		O 16		F 19				(Na 23)
III	Na 23		Mg 24		Al 27.4		Si 28		P 31		S 32		Cl 35.5					
IV		K 39.1		Ca 40		Ga 69.9		Ti 50		V 51.2		Cr 52.2		Mn 55	Fe 56	Co 59	Ni 59	Cu 63
V	(Cu 63)		Zn 65.1						As 75		Se 79		Br 80					
VI		Rb 85		Sr 87.6		?Yt 88		Zr 89.6		Nb 94		Mo 96			Ru 104	Pd 106	Rh 104	Ag 108
VII	(Ag 108)		Cd 112		In 113.5		Sn 118		Sb 122		Te 125?		I 127					
VIII		Cs 133		Ba 137		?Di 138		?Ce 140							?Da 150			
IX																		
X						?Er 178		?La 180		Ta 182		W 184			Os 195?	Pt 198	Ir 197	Au 199
XI	(Au 199)		Hg 200,		Tl 204		Pb 207		Bi 210									
XII								Th 231				U 240						

CHAPTER XI.

THE ALKALI METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	FUSING POINT. °C.	DISCOVERER.
Lithium	Li	7	0.578	180°	Arfwedson, 1817.
Sodium	Na	23	0.97	95°.6	Davy, 1807.
Potassium	K	39.1	0.865	62°.5	Davy, 1807.
Rubidium	Rb	85.4	1.52	38°.5	Bunsen, 1860.
Caesium	Cs	133			Bunsen, 1860.
Ammonium	NH_4	18			
Silver	Ag	108	10.57	1023°	

350. The metals of this group are all monads, forming but one chloride, RCl. The first five—lithium, sodium, potassium, rubidium, and caesium—are the alkali metals. The salts of the hypothetical ammonium are very like those of potassium, and hence it is convenient to study them at this place. Silver is not an alkali metal, but may be reckoned as a sub-group. Some of its salts are isomorphous with those of sodium.

351. The alkali metals have the following properties in common: (1) They may be obtained by the electrolysis of their fused chlorides.

(2) They are soft, light, easily fusible metals which volatilize at high temperatures.

(3) When freshly cut, they possess a strong metallic luster; but, when exposed to the air, they soon tarnish and form white oxides of the formula R_2O. Their affinity for oxygen increases with their atomic weight. When caesium is set free by electrolysis, it takes fire as soon as it is exposed to the air; and hence it has not as yet been obtained except as an amalgam.

(4) Owing to their strong affinity for oxygen, these metals decompose water at all temperatures, setting free its hydrogen. The oxides thus formed dissolve in the excess of water to form hydrates of the formula R_2O, H_2O or RHO. These hydrates can not be deprived of their water by heat alone.

(5) The alkaline hydrates are the strongest bases known, completely neutralizing every acid. They change infusions of red cabbage or violets to green; turmeric, to brown; and restore litmus, which has been reddened by acids, to blue. In a concentrated form they destroy animal and vegetable tissue, acting "caustic." Their taste is acrid and unpleasant.

(6) When these hydrates are exposed to the air they form white carbonates. These alkaline carbonates can not be decomposed by heat alone. They are all soluble in water (lithium somewhat sparingly), and their solutions react alkaline to test papers.

(7) All these elements are very widely diffused, although none of them are found native. Their chlorides are found in very many mineral springs, and are frequently associated together. They are also found in the ashes of many plants, and not unfrequently in minerals. Nevertheless, only sodium and potassium are found in large quantities.

SODIUM.

352. Sodium, Na, is the most abundant of the alkali metals. It is distributed very widely. As a chloride

(NaCl), it is found in the sea water, in salt springs, and in both vegetables and animals. It is also found in many minerals, as rock salt, Chili saltpeter ($NaNO_3$), and some silicates.

353. The metal was first prepared by Davy, in 1807, by electrolysis. It is now prepared on a large scale by heating an intimate mixture of dry sodium carbonate with charcoal to a white heat: $Na_2CO_3 + 2C = Na_2 + 3CO$. At this temperature the carbon reduces the sodium, which distills over and is collected under petroleum. It is then purified by remelting under a thin layer of petroleum, and is cast into bars.

354. Physical properties. Sodium is a silver-white metal, with a brilliant luster when freshly cut, soft like wax, and easily moulded by the hand. Its specific gravity is a trifle less than that of water. It oxidizes rapidly even in dry air, and must be kept under petroleum. When thrown upon water, it decomposes it readily; but the heat evolved is not generally sufficient to enkindle the hydrogen set free.

Exp. 182.—Place a bit of filter paper on the surface of the water, and upon it a pellet of sodium. The sodium will be prevented from rotation, and will oxidize so rapidly as to ignite the hydrogen. The yellow color of the flame is due to the sodium vapor which is simultaneously burned. The water contains sodium hydrate, and reacts alkaline to turmeric paper and to reddened litmus.

355. Sodium is a powerful reducing agent, and is largely used in the preparation of aluminium and magnesium. Its amalgam has recently been employed in the reduction of silver ores.

Exp. 183.—Shake together in a test tube a piece of sodium with an equal bulk of mercury. The two metals will combine with a sharp flame, and, on cooling, form a solid mass (sodium amalgam). This may be employed in reducing silver chloride, or reserved for experiments. (See **Exp. 189**).

356. The salts of sodium are, perhaps, the most important known to chemists. Almost every acid forms a sodium salt, easily soluble in water, and crystallizing from concentrated solutions in well-defined forms. Some of these have received a wide application in the arts, and therefore require a more extended notice than we shall be able to give to those of the metals following.

357. Sodium chloride, $NaCl$, is our *common salt* used in cooking. It is found in Europe in enormous quantities as rock salt. In the United States it is generally obtained by evaporating the waters of salt springs. Millions of tons are manufactured annually from the salt springs of New York, Michigan, Ohio, and West Virginia.

Sodium chloride is about equally soluble in cold and hot water. A saturated brine contains about 26 per cent of salt. From such saturated solutions the salt crystallizes out in beautiful cubes, which sometimes are so attached by their edges as to form hopper-shaped masses. This peculiarity is common to all of the halogen compounds of the alkalies.

The uses of salt as a condiment and in preserving meats are well known. It also finds some employment as a cheap glazing for pottery, and is the source from which most of the other salts of sodium are obtained.

358. Sodium sulphate, Glauber's salt, $Na_2SO_4 + 10H_2O$, occurs frequently in mineral springs, and is used in medicine. It is manufactured in enormous quantities by heating sodium chloride with sulphuric acid. In this process immense quantities of hydrochloric acid are evolved, which are absorbed by passing the gas through towers filled with coke over which a stream of water is constantly trickling. The operation has two stages: (1) The acid first forms an acid sodic sulphate, at a comparatively low temperature; thus, $NaCl + H_2SO_4 =$

$NaHSO_4 + \overset{\frown}{HCl}$. (2) The temperature is then raised, when the acid sodic sulphate acts upon the remaining portion of the salt to form the normal sulphate, $NaCl + NaHSO_4 = Na_2SO_4 + \overset{\frown}{HCl}$. The product thus formed is salled *salt-cake.* If dissolved in water and crystallized out at ordinary temperatures, it retains ten molecules of water and forms monoclinic prisms which effloresce in dry air.

Exp. 184.—When a solution of this salt, saturated at 33° C., is left undisturbed to cool, it forms a so-called supersaturated solution which may be kept for days without crystallizing. If, after cooling, a crystal of the salt be dropped into the solution, the whole solidifies to a mass of the ordinary crystals, with a marked increase of temperature.

359. Sodium carbonate, Na_2CO_3, is made by roasting salt-cake with about an equal weight of chalk and a little more than half its weight of coal.

The chemical change consists mainly, (1) in the action of the carbon upon the sodium sulphate, whereby sodium sulphide is formed: $Na_2SO_4 + 4\,C = Na_2S + 4\,\overset{\frown}{CO}$. (2) In the action of the carbon upon the chalk, whereby the calcium carbonate becomes calcium oxide: $CaCO_3 + C = CaO + 2\,\overset{\frown}{CO}$. (3) When this resulting mass of sodium sulphide, calcium oxide, and unaltered calcium carbonate is treated with water, there forms an insoluble oxy-sulphide of lime, and sodium carbonate is dissolved out: $2\,Na_2S + CaO + 2\,CaCO_3 = 2\,Na_2CO_3 + CaO, 2\,CaS$. (4) The solution thus obtained is allowed to stand, and forms crystals of the formula $Na_2CO_3 + 10\,H_2O$. These crystals easily effloresce, losing their water of crystallization and becoming anhydrous Na_2CO_3.

360. The "bicarbonate" of soda, $Na_2O, H_2O, 2\,CO_2$ or $NaHCO_3$, or acid sodium carbonate, is easily formed by passing into a solution of sodium carbonate a stream of carbonic anhydride.

Sodium carbonate is largely used in the manufacture of glass and of soap, and is the usual *sal-soda* of commerce. Sodium bicarbonate is used in medicine, and is one of the constituents of most baking powders.

361. Sodium hydrate, NaHO, is formed by heating sodium carbonate with an excess of slaked quicklime.

$$Na_2CO_3 + Ca(HO)_2 = 2NaHO + CaCO_3.$$

A considerable quantity is always formed in the process given in § **359,** because of the excess of the chalk and coal used. When its solution is evaporated to dryness, it forms a white, solid, fusible mass, soluble in water, with considerable evolution of heat. It is a very strong base, acting very caustic upon the skin, and readily combining with oils to form hard soaps.

362. Sodium nitrate, $NaNO_3$, is found in large quantities in Peru. It is used in the manufacture of blasting powder; but as it readily deliquesces in moist air, it can not be employed for the manufacture of ordinary gunpowder. It finds an extensive use in the manufacture of ordinary saltpeter, nitric acid, and fertilizers.

363. Di-sodium phosphate, $Na_2HPO_4 + 12H_2O$, is obtained by adding sodium carbonate to phosphoric acid or to its lime salt. It crystallizes in rhombic prisms, which effloresce in dry air. The salt dissolves in four parts of cold water, and yields a solution feebly alkaline. There are several other sodium phosphates.

364. The sodium silicates are also very numerous, and, at the same time, a very interesting set of compounds. When caustic soda and quartz sand are fused together, a silicate of soda is formed. The formula of the resulting compound will vary with the proportions used, as silicic acid possesses in a wonderful degree the property of forming the so-called "condensed" salts. The "water glass" of commerce has very nearly the formula $2Na_2O, 5SiO_2$. It is soluble in water, and is used for the preparation of artificial stone, for the manufacture of fire-proof paints, and is also used in some kinds of soap.

POTASSIUM.

365. Potassium resembles sodium in most of its properties, and is frequently found associated with it in nature. It exists in sea water; in many mineral springs as KCl. Large deposits of the solid chloride have recently been discovered at Stassfurth. It is also a constituent of the common feldspars and micas. These minerals, decomposing through atmospheric influences, become important agents in soils, and yield their potash to growing plants. From these it is again transferred to animals, and becomes an important constituent of milk, blood, and flesh.

The principal source from which the potassium compounds are obtained is the ashes of plants. When a plant is burned, the organic salts of potash are decomposed and the carbonate is formed. This is exhausted by water, and forms *potash lye.*

366. The manufacture of the metal is effected by heating its acid tartrate in closed iron retorts.

(1) At a low heat, the tartrate is converted into an exceedingly intimate mixture of potassium carbonate and charcoal. (2) This mixture is then raised to a white heat; the metal is reduced and distills over: $K_2CO_3 + 2C = 2K + 3CO$. (3) The product is received under petroleum. It is contaminated with a black, explosive compound of potassium and carbonic oxide, and requires to be again distilled in order to obtain the metal in a pure state.

367. Potassium is a soft metal, having a bluish tinge and a brilliant luster. At 0° C., it is brittle; at ordinary temperatures it may be moulded like wax, and two fresh surfaces easily welded together. It melts at 62.5° C., and at a red heat volatilizes with a beautiful green vapor.

It is one of the lightest of metals: sp. gr. 0.86.

It is strongly electro-positive, and exhibits a remarkable affinity for oxygen. When exposed to dry air, its surface becomes almost immediately covered with the protoxide K_2O. It decomposes water at all temperatures, and with sufficient energy to ignite both itself and the hydrogen set free. The flame produced is a rich violet, and is characteristic.

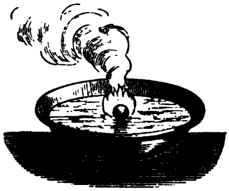

FIG. 88.

Owing to the expense of manufacturing potassium, it is not employed in the arts, being replaced by its congener sodium.

Exp. 185.—Make a small cavity in a lump of ice, and drop in this a small pellet of potassium. It will take fire and burn. Test the liquid remaining after the potassium has disappeared. It contains potassium hydrate and reacts alkaline.

$$H_2O + K = KHO + H.$$

Exp. 186.—The strong affinities of potassium may be further shown by (1) placing a dried pellet in a deflagrating spoon, (2) melting the metal, and then (3) plunging it into various gases; as, CO_2, Cl, H_2S. It decomposes carbonic anhydride, setting free its carbon, and combines with chlorine with evolution of light.

368. Compounds of potassium. When the ashes of plants are lixiviated with water, a dark-colored lye is obtained which contains all the soluble salts of the ash. This lye, boiled down to dryness, constitutes the crude "potash" of commerce. It consists mainly of potassium carbonate; it also generally contains some potassium sulphate and some sodium salts.* If the dark color of crude potash is destroyed by roasting, it forms "pearl ash." Pure potassium carbonate is best obtained by igniting the acid tartrate or oxalate.

369. Potassium carbonate, K_2CO_3, is a white, deliquescent salt, very readily soluble in water. It has a strong alkaline taste and reaction.

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* In some American potashes there exists a very considerable amount of sodium carbonate.

It was formerly of greater importance in the arts than now; but is still very largely used in the preparation of soft soap, of some kinds of glass, and in the preparation of other salts of potassium.

370. The acid potassium carbonate, $KHCO_3$, is formed by passing carbonic anhydride through a solution of the preceding in four parts of water. Beautiful monoclinic prisms soon separate out. It was formerly much used, under the name of saleratus, in baking powders and in effervescing drinks.

When the acid carbonate is heated, it loses water and half of its carbonic acid, and returns to the state of a normal carbonate. No amount of heat will expel the carbonic acid remaining. If, however, its not too concentrated solution is treated with quicklime, it is decomposed and yields

$$K_2CO_3 + Ca(HO)_2 = CaCO_3 + 2KHO.$$

371. Potassium hydrate, KHO. The solution thus formed is poured off and evaporated to dryness in iron or silver vessels. The solid hydrate is a hard, brittle, white, deliquescent mass, fusible below red heat. It readily absorbs carbonic anhydride from the air; but as it is soluble in alcohol, while the carbonate is not, an alcoholic solution of a partially altered mass will contain only the hydrate.

It is one of the strongest bases known, completely neutralizing the strongest acids, and displacing most other bases from their salts. Its taste is nauseous, and its solution, when concentrated, is highly corrosive to organic tissues. It is employed in medicine as a caustic, whence it is called *caustic potash.* It combines with fats to form soft soaps.

Exp. 187.—Add a solution of potassium hydrate to any salt of iron or copper. The iron or copper oxide will precipitate, and the potash remain in solution, combined with the acid of the salt.

372. Potassium chloride and potassium chlorate are formed when a solution of potassium hydrate is treated with chlorine. The reaction has already been described (Art. **136**). The Stassfurth carnallite ($MgCl_2, KCl + 6H_2O$) promises to be an abundant source for the manufacture of potassium carbonate. The process is similar to that described for the preparation of sodium carbonate.

Similarly, potassium bromide and potassium iodide are formed when bromine and iodine are added to solutions of potassium hydrate until the solution becomes very slightly colored: $6Br + 6KHO = 5KBr + KBrO_3 + 3H_2O$. Small quantities of bromates or iodates are formed at the same time. These may be separated out by crystallization, or decomposed by heating into oxygen and the halogen salts.

All these salts (KCl, KBr, KI) crystallize in cubes like common salt, and have a pleasant saline taste. The two latter are largely employed in medicine and in photography.

373. There are five potassium sulphides. We shall describe two only. If sulphuretted hydrogen gas is passed into potash lye to full saturation, the sulphydrate is formed: $KHO + H_2S = KHS + H_2O$. If this solution is mixed with an equal quantity of the potash lye, the monosulphide is formed: $KHS + KHO = K_2S + H_2O$. Both of these salts, when treated with acids, evolve sulphuretted hydrogen, and are used to form sulphides of many of the metals in the wet way. They are strong sulphur bases, and easily combine with the sulphides of arsenic, antimony, and tin to form soluble sulphur salts.

374. Potassium nitrate, KNO_3, saltpeter, occurs naturally in the soils of many hot countries, and as an efflorescence in some caverns. It is formed artificially by the oxidation of nitrogenous organic bodies in the presence of strong bases like lime. Large heaps of organic matters, mixed with old mortar and lime, are freely exposed to the air, but protected from rain by a roof. These heaps are moistened from time to time with stable drainings, and finally lixiviated. The resulting calcium nitrate, when treated with potassium carbonate, yields potassium nitrate. It is now abundantly prepared by boiling together solutions of Chili saltpeter and potassium chloride: $NaNO_3 + KCl = KNO_3 + NaCl$. The sodium chloride first crystallizes out, and then the saltpeter, in long six-sided prisms.

The principal use of saltpeter is in the manufacture of fireworks and gunpowder.

Its taste is saline and cooling. When heated, it melts at 340° C., and then decomposes into oxygen and potassium nitrite. From the ease with which it gives up its oxygen, it is a powerful oxidizing agent.

Exp. 188.—Ignite a piece of charcoal and throw upon it a little saltpeter: it will deflagrate brilliantly.

375. Gunpowder is an intimate mixture of about 75 parts of saltpeter, 13 parts of sulphur, and 12 parts of charcoal. This amounts very nearly to $2KNO_3 + S + 3C$. It must, however, be remembered that it is not a compound, but a mixture. The materials are (1) pulverized, thrown together, moistened, and thoroughly mixed by grinding under an edge mill. (2) It is then subjected to great pressure, whereby it forms a compact mass. (3) This is broken in pieces of different sizes, which are sorted by sieves. (4) The powder is then dried by steam heat, and is frequently glazed with plumbago.

When gunpowder is fired, its explosive force is due to gaseous products such as CO_2, CO, N, and O; but besides these there are many solid products, as K_2SO_4, K_2CO_3, K_2S, etc.

Saltpeter has also some power as an antiseptic, and is used in the manufacture of nitric acid.

376. Potassium sulphate, K_2SO_4, is a by-product in the manufacture of nitric acid. When an excess of sulphuric acid is used, the acid potassium sulphate $KHSO_4$ forms. The latter, heated to about 200° C., gives off water and forms the so-called anhydrosulphate $K_2S_2O_7$ or SO_3, K_2, SO_4. At a still greater heat, sulphŭric anhydride is evolved, leaving the normal sulphate K_2SO_4.

377. Caesium and rubidium are very widely distributed in mineral waters and the ashes of many plants, but, nevertheless, in exceedingly small quantities. More strongly electro-positive than potassium, they resemble it in most particulars, but are distinguished from it by the greater insolubility of their salts, and the colors which their salts yield in the spectrum. (See Art. 417).

AMMONIUM.

378. When a solution of ammonia in water is neutralized by an acid, a salt is formed which is very similar to the corresponding salt of potassium. It is convenient to consider that these salts contain a monatomic radical *ammonium*, NH_4, which acts like an atom of potassium, although this radical has never been isolated. (See Art. **204**).

Exp. 189.—Add to a strong solution of ammonium chloride a pellet of sodium amalgam. (Exp. 183). A bulky mass of the consistence of butter forms, which was once thought to be ammonium amalgam, NH_4Hg'. However, it differs in many respects from sodium amalgam, and soon decomposes into mercury, free ammonia, and hydrogen.

379. The solution of ammonia in water may be regarded as NH_4HO, ammonium hydrate, or aqua ammonia. It corresponds in most of its chemical reactions to potassium hydrate, but has never been obtained in the solid state. It smells strongly of ammonia, and readily gives off this gas upon boiling.

380. When nitrogenous bodies decay, or when horns, bones, etc., are subjected to destructive distillation, an impure ammonium carbonate is formed. The same product is found in the ammoniacal liquors obtained in the manufacture of illuminating gas from coal. These liquors are now the chief source of ammonium salts. When treated with quicklime, they yield gaseous ammonia; with sulphuric acid, ammonium sulphate; with hydrochloric acid, ammonium chloride.

381. The ammonium chloride, NH_4Cl, thus formed is purified by first evaporating the liquid to dryness, and then heating the dried product. The ammonium chloride sublimes without previous melting, and collects in tough, fibrous masses in the receiver. It dissolves in its own weight of water at 100° C., and, on cooling, crystallizes out in white, feathery aggregations of cubes or octahedra.

It is an interesting fact that the vapor of ammonium chloride has but half the density due to theory (1.86). To account for this, it is supposed that the vapor (two molecules) is decomposed into two volumes of NH_3 and two of HCl, no longer combined, and therefore not condensed. This phenomenon is called *dissociation.* On cooling, the two gases again combine.

Ammonium chloride is extensively used in medicine. It dissolves many oxides, as zinc, and hence is used in soldering. It is also the principal source from which most of the other salts of ammonia are formed.

382. Ammonium carbonate is made by heating a mixture of ammonium chloride and calcium carbonate. The carbonate thus formed is a white, easily soluble mass, strongly smelling of ammonia, having the probable formula of $2NH_4O, 3CO_2 + 3H_2O$. It is the *sal-volatile* of the apothecary.

There are two other carbonates of ammonia. The acid carbonate, NH_4, H, CO_3, forms when the preceding sesquicarbonate is exposed to the air as a white, almost odorless powder, somewhat difficultly soluble in water. The normal carbonate, $(NH_4)_2CO_3$, has never been obtained except in solution.

383. Ammonium sulphate, $(NH_4)_2SO_4$, is important only because it is sometimes used in the manufacture of other ammonium compounds, especially of ammonia alum.

384. Ammonium nitrate, NH_4NO_3, is a deliquescent salt, very easily soluble in water. When the dry salt is heated gradually to about 240° C., it decomposes into nitrous oxide and water: $NH_4NO_3 = N_2O + 2H_2O$.

385. Microcosmic salt, $Na, NH_4, H, PO_4 + 4H_2O$, is of great importance in blowpipe operations. When heated, it first loses its water, then its ammonia, and becomes a glassy, transparent mass of sodium metaphosphate, which has the property of dissolving many metallic oxides with characteristic colors.

386. Ammonium sulphide, $(NH_4)_2S$, is prepared by saturating aqua ammonia with sulphuretted hydrogen, and then adding an equal quantity of aqua ammonia.

$$(1)\ (NH_4)HO + H_2S = NH_4HS + H_2O.$$
$$(2)\ NH_4HS + NH_4HO = (NH_4)_2S + H_2O.$$

When first prepared it is very nearly colorless, but gradually becomes yellow, or even red, by reason of the formation of higher sulphides. By long standing it is fully decomposed, with separation of white sulphur. It is a very important agent in analytical chemistry.

Exp. 190.—Add $(NH_4)_2S$ to a solution of a zinc salt. White ZnS separates out.

Exp. 191.—Add $(NH_4)_2S$ cautiously to a solution of tartar emetic. At first, an orange sulphide of antimony precipitates; but, on adding more $(NH_4)_2S$, it redissolves to form the sulphantimonite $(NH_4)_2S, Sb_2S_3$.

387. Ammonium bromide, NH_4Br, and ammonium iodide, NH_4I, are colorless, crystallizable salts, which are extensively used in photography and have some employment in medicine.

LITHIUM.

388. Lithium is the lightest of the metals, floating even upon naphtha. It occurs in many minerals and mineral springs; notably in a spring in Cornwall, England, which yields daily 800 pounds of lithium chloride.

In its general properties it resembles sodium, but the sparing solubility of its carbonate and phosphate ally it to magnesium. It may, therefore, be regarded as a connecting link between the alkalies and the alkaline earths.

Its citrate and carbonate are used in the treatment of rheumatism.

Tests for the Alkalies.

(1) All alkaline salts, when boiled with milk of lime, yield solutions of alkaline hydrates. These solutions turn turmeric paper brown, and restore the color of reddened litmus. Ammonia alone yields a volatile product, which may be recognized by its peculiar odor, and by its yielding white fumes in the presence of strong hydrochloric acid.

(2) In solutions not too concentrated, lithium alone yields a precipitate with sodium di-phosphate and sodium carbonate.

(3) In moderately strong solutions, an excess of tartaric acid yields, with salts of NH_4, K, Cs, and Rb, white crystalline precipitates of acid tartrates, somewhat freely soluble in boiling water.

(4) In solutions acidified with HCl, platinum tetrachloride, $PlCl_4$, yields yellow crystalline precipitates of the formula $2RCl, PtCl_4$, with salts of NH_4, K, Cs, Rb.

(5) K, Cs, Rb, Li, and Na, when heated in a non-luminous flame, tinge the flame with characteristic colors, which have fixed places in the spectrum. (See Spectrum Analysis).

SILVER.

389. This beautiful metal not unfrequently occurs native. Its most abundant ore is the sulphide; but this is generally associated with other sulphides, as those of arsenic, antimony, and lead. It occurs less frequently in combination with Cl, Br, and I.

390. The method of extracting silver from its ores depends upon the character of the minerals with which it is associated. The so-called *amalgamation* process is, perhaps, the most common. The sulphides are (1) roasted with common salt, whereby all the silver is converted into silver chloride. (2) The resulting mass is then mixed with iron scraps and water, and placed in huge wooden casks which are made to revolve by machinery. The silver is reduced to the metallic state, $2AgCl + Fe = FeCl_2 + 2Ag$. (3) Mercury is then added in sufficient quantity to form a fluid silver amalgam, which is then drawn off from the earthy matters remaining, and washed. (4) The excess of mercury is pressed out, and the remaining amalgam heated in iron retorts. The mercury distills over, and metallic silver (often containing gold) remains behind.

391. The silver produced in Europe is obtained principally from galena, PbS, which very generally contains silver. By Pattison's process, lead ores containing not more than three ounces to the ton can be profitably worked. (1) On smelting the ores, all the silver is obtained as an alloy with the lead. (2) This alloy is melted in large iron kettles and allowed to cool gradually. Crystals of lead form, which are removed by iron strainers. (3) This process is repeated with the residue until a rich alloy of silver is obtained. (4) The final process is by *cupellation*, which consists in oxidizing the lead in a shallow vessel made of bone ash, by a flame which is made to play over its surface. The lead oxide (litharge) is partly driven away and partly sinks into the cupel, while pure silver remains behind.

392. Pure silver does not oxidize in the air; but, when in the melted state, has the curious property of absorbing 22 volumes of oxygen. When the metal cools, the oxygen escapes and bursts through the solidified crust, giving rise to the phenomenon called the "spitting of silver." Pure silver is quite soft, and is never used in the arts. Silver plate and coins contain ten per cent of copper.

Pure silver may be prepared from coin by (1) dissolving in nitric acid; (2) precipitating the silver, as $AgCl$, by hydrochloric acid; and (3) reducing the thoroughly washed silver chloride by zinc. Thus prepared, it is a brown powder which may be melted at 1000° C. into a solid mass.

Silver is the whitest of the metals, very malleable and ductile, and the best conductor of heat and of electricity. It readily blackens in air containing sulphuretted hydrogen, owing to the formation of silver sulphide. It is scarcely acted upon by hydrochloric acid; but, when heated with strong sulphuric acid, dissolves, forming a silver sulphate sparingly soluble in water: $2Ag + 2H_2SO_4 = 2H_2O + SO_2 + Ag_2SO_4$. Its best solvent is nitric acid, with which it forms

$$4Ag + 6HNO_3 = 3H_2O + N_2O_3 + 4AgNO_3.$$

393. Silver nitrate, $AgNO_3$. This salt crystallizes in anhydrous, rhombic plates. These melt at 219° C., and form, on cooling, a hard mass which is used by surgeons under the name of *lunar caustic.* When moistened and applied to the flesh, it quickly and completely destroys the vitality of the part. When pure, it is not altered by sunlight; but, when in contact with organic matters, soon blackens and is reduced to the metallic state.

Hence, it stains the skin black; and hence, also, its use as an ingredient of indelible ink and of many hair dyes. It is the only salt of silver freely soluble in water, and is used to prepare most of the other silver salts. Sodium hydrate added to its solution precipitates

394. Silver oxide, Ag_2O, a brown, amorphous powder, which is a strong base, but is decomposed by heat into oxygen and metallic silver.

395. Silver chloride, $AgCl$, is readily formed from a solution of silver nitrate, by adding to it HCl or any soluble chloride. It forms a white, curdy precipitate, insoluble in nitric acid, but soluble in ammonia and in sodium hyposulphite. On exposure to sunlight, it rapidly blackens, losing chlorine and forming, as is probable, a sub-chloride of silver, Ag_2Cl. Whatever be the change, the blackened chloride is no longer soluble in sodium hyposulphite. The art of producing photographs upon paper is largely dependent upon this molecular change.

396. Silver bromide, $AgBr$, is prepared by adding to the solution of the nitrate any soluble bromide, as KBr. It has a yellowish tinge, and is somewhat sparingly soluble in ammonia, and less sensitive to light than the chloride.

397. Silver iodide, AgI, precipitates as a yellow powder almost insoluble in ammonia, when a soluble iodide, as KI, is added to a solution of silver nitrate. On exposure to light, it is scarcely altered in color, loses no iodine, but suffers an unexplained molecular change.

398. Photography, as now practiced, consists essentially of two processes: (I) the preparation of a negative picture on glass; (II) the printing of positive pictures from this upon paper.

I. (1) A clean plate of glass is thinly coated with a solution of collodion containing various bromides and iodides, as CdI, NH_4I, NH_4Br. This rapidly dries, and forms a thin but coherent film upon the glass. (2) The plate is then dipped in a solution of silver nitrate, whereby a sensitive film of silver iodide and bromide is formed. (3) It is then exposed in a camera for a few seconds. The film does not suffer any visible alteration, but some molecular change takes place, in consequence of which a latent image is formed. (4) This latent image is *developed* by pouring upon the film a solution of ferrous sulphate. The ferrous sulphate reduces the silver, which has been acted upon by the light, and forms a *negative* picture; that is, one in which the lights and shades of an ordinary drawing are reversed. (5) The plate is then protected from the further action of light by washing in a solution of sodium hyposulphite, to remove the unchanged silver salts, and then in a large quantity of water. (6) The film is finally coated with a thin film of varnish to protect it from injury.

II. To obtain a positive picture upon paper, or one in which the lights and shadows are in their natural positions, (1) a sheet of white paper is coated upon one side with a layer of albumin containing ammonium or sodium chloride. (2) This paper is rendered sensitive by washing with a solution of silver nitrate, which is thereby converted to silver chloride. (3) The paper thus prepared is placed, when dry, behind a negative picture and exposed to the sunlight. (4) The exposed portions of the chloride are reduced and blacken, forming a positive picture. (5) It remains now only to dissolve out the unaltered chloride by sodium hyposulphite and water, in order to render the picture permanent; but, (6) as the silver thus reduced has an unpleasant red color, the picture is "toned," to give it a more agreeable tint. This is effected by steeping the paper in a solution containing a little gold chloride until the desired tint is obtained. (7) Finally, it is again washed, dried, and mounted.

399. Positive pictures may also be obtained upon glass, by a short exposure in the camera, and not too strong development. They are then placed upon a dark background. The reduced silver conceals the black ground and reflects the lights, while the transparent portions allow the black ground to show through, and thus represent the shadows of the picture.

TESTS.—Most silver salts are insoluble in water, and hence a solution of silver nitrate yields precipitates with phosphates, arsenites (yellow); arseniates, chromates (red); oxalates, chlorides, bromides, iodides (white or yellowish); and sulphides (black). All of these except the last two (AgI and Ag_2S) are soluble in ammonia.

A sufficient test for silver in its solutions is obtained by adding HCl to them. The white, curdy AgCl is characteristic.

Insoluble silver compounds, mixed with dry sodium carbonate and heated upon charcoal, yield a globule of metallic silver, which may be dissolved in nitric acid and tested in the wet way — by $K_2Cr_2O_7$, HCl, and NH_4HS.

Recapitulation.

Review § 351.

The alkali metals closely resemble each other in their physical properties.

As a general rule, their specific gravities, electro-positive characters, and the basicity of their hydrates increase with their atomic weights: their melting points decrease.

Their salts are generally soluble in water.

In most chemical reactions, the compounds of any one of them (and of ammonium) may take the place of any corresponding compound of any other: allowance must, however, be made for difference in solubility.

Silver differs essentially from the alkalies in its high specific gravity and melting point, as well as in its weak affinity for oxygen, and the difficult solubility of most of its salts in water.

CHAPTER XII.

THE DYAD METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	FUSING POINT. °C.	VOLATILIZES. °C.	DISCOVERER.
Calcium	Ca	40	1.58			Davy, 1808.
Strontium	Sr	87.5	2.5			Davy, 1808.
Barium	Ba	137	4.	450°		Davy, 1808.
Lead	Pb	207	11.4	325°		
Magnesium	Mg	24	1.74	433°		Bussy, 1829.
Zinc	Zn	65	7.1	412°	1040°	
Cadmium	Cd	112	8.7	320°	860°	Stromeyer, 1818.
Mercury	Hg	200	13.6	—39°.4	350°	
Copper	Cu	63.4	8.9	1200°.		

400. Calcium, strontium, and barium form a group with gradational properties not less well defined than that of the alkalies.

These metals have been obtained only in small quantities by the electrolysis of their fused chlorides. They are moderately hard, yellowish metals, fusible below red heat. Although less easily oxidized than the alkali metals, they decompose cold water, forming hydrates; as, CaO, H_2O or $Ca(HO)_2$. These hydrates are sparingly soluble in water (barium hydrate, the most readily; calcium hydrate, the least), forming solutions which have a weak alkaline reaction. Unlike the alkaline hydrates, these hydrates may be decomposed by heat into water and white anhydrous oxides, as CaO. These oxides are all strong bases, their basicity increasing with their atomic weights (barium being the most electro-positive, and calcium the least). They saponify fats, but form insoluble soaps.

These elements also differ from the alkalies in the fact that their carbonates are decomposed by heat, yielding carbonic anhydride and the anhydrous oxides. The carbonates, phosphates, and sulphates are either insoluble in water or very sparingly soluble ($CaSO_4$).

Their chlorides have the formula RCl_2, and hence these metals are dyad. The chlorides of calcium and strontium are deliquescent salts easily soluble in water and in alcohol. Barium chloride is not deliquescent and is not soluble in alcohol.

401. Lead is added to this group because many of its salts are similar to those of barium. Its carbonate, phosphate, and sulphate are insoluble in water. It acts as a dyad metal in most of its compounds, as $PbCl_2$, PbO; but sometimes acts as a tetrad, especially in some organic compounds, as $Pb, (C_2H_5)_4$, plumbic ethide.

CALCIUM.

402. The compounds of calcium are very widely and abundantly distributed. They occur in enormous quantities as carbonates, in marble, chalk, and limestone; as sulphates, in gypsum and alabaster; as silicates, in many minerals, *e.g.* labradorite; and less frequently as fluorides, in fluor spar. It is also an almost invariable constituent of vegetables and animals, being especially concentrated in shells, corals, teeth, and bones.

403. Calcium carbonate, $CaCO_3$, has a great variety of crystalline forms which are referable to two systems: (1) the hexagonal, represented by Iceland spar; (2) the trimetric, represented by aragonite. It is found in the ashes of plants, in egg-shells, in bones, corals, and in the shells of mollusks. The enormous masses of limestone, which serve as building stones, are largely made up of the broken and pulverized forms of the two latter. It is prepared artificially by adding ammonium carbonate to a solution of calcium chloride.

Calcium carbonate is almost insoluble in water. Waters containing free carbonic anhydride dissolve it more freely, forming the so-called calcareous mineral waters. They contain, probably, acid calcium carbonate, $CaH_2(CO_3)_2$. This salt has not been obtained in the solid state, because, when these waters are evaporated, they lose a molecule of carbonic anhydride, and yield a precipitate of calcium carbonate. Hence, such mineral waters deposit naturally, on exposure to the air, their calcium carbonate, forming tufa, stalactites, etc., or yield it up upon boiling, forming the incrustations of boilers. Such waters are said to have a "temporary hardness." This hardness is removed by boiling, or by the addition of calcium hydrate in sufficient quantity to form the insoluble normal carbonate.

Exp. 192.—(1) Pass into a solution of calcium hydrate, diluted with an equal amount of water, a stream of carbonic anhydride: calcium carbonate precipitates. (2) Continue the operation, and the calcium carbonate again dissolves. Now divide the product into two parts. (3) Boil one, and observe that it soon becomes turbid. (4) To the other portion add, gradually, a solution of calcium hydrate, and observe the same turbidity, being in both cases due to precipitated calcium carbonate. Upon the latter reaction rests Clark's process of softening calcareous waters.

404. Calcium oxide, CaO, or quicklime, is formed when calcium carbonate is heated to redness in the open air.

It is a white, amorphous, infusible mass. When water is poured upon quicklime, the two combine quickly with great evolution of heat, and the quicklime crumbles to a white powder, which is calcium hydrate: $CaO + H_2O = Ca(HO)_2$. This is the *slaking* of lime. When exposed to the air, quicklime gradually absorbs moisture and forms air-slaked lime. Calcium hydrate dissolves in about 700 parts of cold water to form a feebly alkaline and caustic solution. It readily absorbs carbonic acid, and is used as a test for it.

405. Calcium hydrate suspended in water forms "milk of lime." Its caustic property, together with its strong affinity for carbonic anhydride, renders it a useful agent (1) in tanning, to remove hair from hides; (2) in forming, with fats, insoluble soaps, which are afterward employed in preparing stearine candles; (3) in the preparation of caustic alkalies; (4) in purifying coal gas. (5) When mixed with sand, it is ordinary mortar. This, as it dries, becomes a mixture of calcium carbonate and calcium silicate, capable of binding stones and bricks firmly together. Hydraulic cements, which have the property of hardening under water, contain from 15 to 30 per cent of alumina and silica (clay), and frequently some magnesia. (6) It is also largely used in the manufacture of the "chloride of lime," used in bleaching cotton goods. The process consists simply in passing chlorine gas over slaked lime, whereby a calcium chloride and hypochlorite are simultaneously formed,

$$2Ca(HO)_2 + Cl_4 = (CaCl_2 + CaClO)_2 + 2H_2O;$$

always, however, mixed with an excess of calcium hydrate. This mixture, treated with water, yields an impure solution of calcium hypochlorite, which, when treated with dilute acids, yields either hypochlorous acid or free chlorine, and is, therefore, a powerful bleaching and disinfecting agent.

When this solution is boiled, the chlorate is formed, $3Ca(ClO)_2 = 2CaCl_2 + Ca(ClO_3)_2$, whence it is economically used in the preparation of potassium chlorate:

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

406. Calcium chloride, $CaCl_2$, which is a by-product in the last process, is more advantageously prepared for laboratory purposes by the action of hydrochloric acid upon calcium carbonate:

$$CaCO_3 + 2HCl = CO_2 + H_2O + CaCl_2.$$

It crystallizes from strong solutions in transparent prisms, $CaCl_2, 6H_2O$. These, mixed with snow, form a freezing mixture, reducing the temperature to — 48° C. (more than sufficient to solidify mercury). When heated to 200° C., they become anhydrous; and, on cooling, form a porous mass extremely deliquescent, and therefore largely employed as a desiccating agent in drying gases.

407. Calcium sulphate, $CaSO_4$, is soluble in about 400 parts of water at ordinary temperatures, and about 460 parts at 100° C. Hence, it is not entirely expelled by boiling, and is one of the causes of the "permanent hardness" of water. It is somewhat more soluble in salt waters; but, when these are evaporated, crystallizes out much sooner than the common salt. In nature we find it frequently associated with beds of rock-salt as gypsum and alabaster, $CaSO_4, 2H_2O$. When gypsum is heated it loses its water of crystallization; and, if not heated beyond 250° C., retains the power of again uniting with the water, and setting to a hard mass. This calcined gypsum is the "plaster of Paris" used in stucco-work, in making casts, and as a valuable fertilizer.

Exp. 193.—(1) Sift *into* a small quantity of water ground plaster of Paris until it rises to the surface. On stirring this it forms a pasty mass. (2) If, now, this is poured into a suitable mould, it "sets," or hardens, at the same time expanding so as to fill every cavity of the mould. (3) In a short time it will be so hardened that it can be removed, and will then present an exact reverse copy or cast of the mould. (4) To prevent the cast clinging to the mould, it is only necessary previously to smear it carefully with oil.

408. Calcium phosphate, $Ca_3(PO_4)_2$, is very widely diffused in soils, though not very abundant. It is taken up by plants, especially by cereals, like wheat, and is the chief inorganic constituent of the bones of animals. (See Arts. **227** and **228**).

COMPOUNDS OF STRONTIUM.

409. Strontium occurs somewhat sparingly in nature as a carbonate, $SrCO_3$ (strontianite), and as a sulphate, $SrSO_4$ (coelestine). These salts are used only as sources of the soluble salts.

The best source of strontium compounds is the carbonate, which is readily soluble in nitric and hydrochloric acids. They are also prepared from the sulphate by (1) roasting it with charcoal, whereby it is converted to a soluble sulphide ($SrSO_4 + 4C = 4CO + SrS$), and (2) dissolving the crude product in hydrochloric or nitric acid, $SrS + 2HNO_3 = H_2S + Sr(NO_3)_2$.

410. Strontium nitrate, $Sr(NO_3)_2$, is readily soluble in water, but is insoluble in alcohol. It is used in fireworks for the preparation of crimson flames. When strongly ignited, it yields *strontium oxide*, SrO, a body similar to quicklime; but, on slaking, is more soluble in water, and yields a more caustic solution. *Strontium chloride*, $SrCl_2$, is freely soluble both in water and alcohol.

BARIUM COMPOUNDS.

411. The principal native compounds of barium are also the carbonate (witherite) and the sulphate (heavy spar). The sulphate is extensively used as a pigment, under the name of "permanent white," in adulterating white lead, and in the manufacture of paper, to give weight.

Its soluble compounds are obtained like those of strontium.

412. Barium nitrate, $Ba(NO_3)_2$, is insoluble in alcohol, but soluble in 12 parts of cold water. It is used in fireworks to prepare green flames. When ignited, it yields *barium oxide*, BaO, which is soluble in 20 parts of cold water, yielding a strongly caustic solution of barium hydrate, $Ba(HO)_2$. It rapidly absorbs carbonic anhydride from the air, and is used for the volumetric determination of that gas.

413. Barium peroxide, BaO_2, is an interesting compound, prepared by heating barium oxide in a current of air or of oxygen. If, now, the temperature be slightly raised, and steam be passed over the peroxide, oxygen will be given off and barium oxide will remain. It is proposed to prepare oxygen on a large scale by using these reactions alternately. (See Art. **114**).

414. Barium chloride, $BaCl_2$, crystallizes in rhombic, non-deliquescent plates. They are soluble in water, but not in alcohol. Its principal use is in the detection of sulphuric acid.

415. All the soluble salts of barium are poisonous. Any soluble sulphate, as Epsom salts, may be given as an antidote.

416. Tests.—Most of the tests for the metals depend upon the fact that certain reagents, when added to their solutions, form new compounds of sparing solubility.

These new compounds, if *insoluble*, separate out at once; if *difficultly soluble*, at once in strong solutions, but only after a time in dilute solutions; if *moderately soluble*, only in somewhat concentrated solutions; if *freely soluble*, not until the solutions are so concentrated by evaporation that the point of crystallization is reached.

The delicacy of such reactions, therefore, depends on the insolubility of the new compound formed.

(1) All carbonates, phosphates, and sulphates of the calcium group are either insoluble or difficultly soluble in water. They are formed as white precipitates when any alkaline carbonate, phosphate, or sulphate is added to solutions of their salts.

(2) Calcium sulphate is soluble in 400 parts of water, and its solution may be used for the detection of Ba and Sr. Barium sulphate is quite insoluble, and strontium sulphate nearly so.

(3) Ammonium oxalate also forms a white precipitate with these salts. When free oxalic or acetic acid is present, only calcium oxalate precipitates. This is a very characteristic test for calcium.

(4) Potassium chromate produces an almost insoluble barium chromate, a moderately soluble strontium chromate, and a freely soluble calcium chromate. Hence, a solution of strontium chromate is a characteristic test for barium.

(5) All these salts tinge a colorless flame with a characteristic color: calcium, brick-red; strontium, crimson; and barium, green. When examined by the spectroscope, these colors yield lines of definite refrangibility.

SPECTRUM ANALYSIS.

417. Most compounds of the alkalies and of the calcium group, are readily volatile. When heated in the almost non-luminous flame of a Bunsen's burner, they yield colored flames which are often sufficiently characteristic to be determined by the eye. If, however, these colored flames are passed through a prism, each flame is found to yield one or more colored lines which have a fixed place in the spectrum, and are therefore characteristic for each element. Upon these facts the spectrum analysis is based.

The spectroscope (Fig. 89) is used for examining colored flames. The substance to be tested is volatilized upon a platinum wire in a Bunsen's burner at E. The flame is passed through a narrow slit in the tube, A, and thrown upon the prism, P. The light is refracted by this prism in rays of definite refrangibility, which fall upon the object-glass of the telescope, B, and pass through it to the eye. In this way, with a single prism and at moderate temperatures, it is found that sodium yields but one yellow line; lithium, a bright red line and a fainter orange; potassium, two lines—one red and the other violet; thallium, one green line. The spectra of the calcium group are more complex. Strontium yields six red lines, one orange, and one blue line; calcium, several lines, two of which, a green and an orange, are especially characteristic; and barium, a large number of green lines.

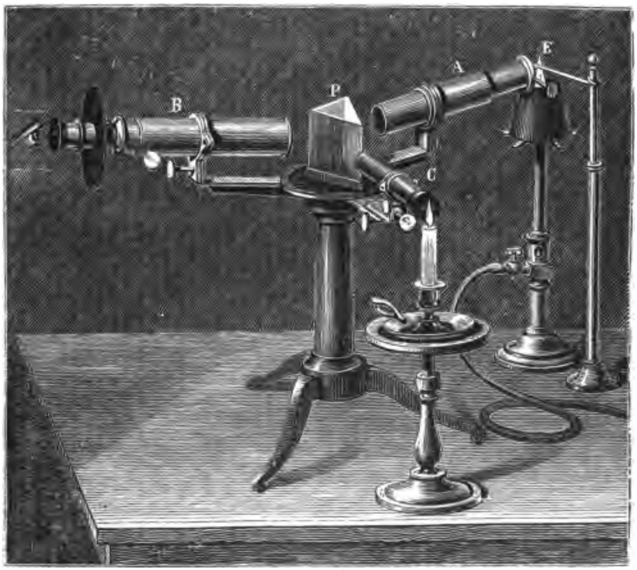

FIG. 89.

In order to fix the place of these lines, a tube, C, is added. It contains at one end a transparent scale of equal parts. When this scale is illuminated by a bright light, it casts a bright image on the prism, which is reflected by the prism into the telescope, B, so that the observer can fix the exact position of the lines produced by the flame which he is examining. In the first scale constructed by Bunsen, the sodium line coincided with the line 50; lithium, with 31 and 45, etc.* It was also found that these lines were always characteristic, and that, in a mixture, each element yielded its characteristic lines, as if it were volatilized alone. No chemical test rivals this in the delicacy of the reaction. Bunsen calculated that he had found $\frac{1}{180000000}$ of a grain of sodium, and could be certain of $\frac{1}{20000}$ of a grain of caesium.

The method here described is the only one used in the chemical laboratory. It must, however, be added that, at higher temperatures (as that of the electric spark), and by using a train of prisms, other lines are found and other metals volatilized, yielding numerous and characteristic lines.

To the invention of the spectroscope we owe the discovery of caesium, rubidium, thallium, indium, and gallium.

LEAD.

418. Many lead compounds occur in nature, but by far the most abundant is the sulphide, or galena, PbS. The reduction of the sulphide is effected in reverberatory furnaces, in which the dressed galena (1) is roasted at a gentle heat in a current of air. The lead sulphide is thereby converted partly into lead oxide and partly into lead sulphate:

$$PbS + 3O = SO_2 + PbO; \quad PbS + 4O = PbSO_4.$$

(2) The furnace is then closed and the temperature raised, whereby the undecomposed sulphide reacts upon the products already formed to produce metallic lead:

$$(1) \quad 2PbO + PbS = SO_2 + 3Pb.$$

$$(2) \quad PbSO_4 + PbS = 2SO_2 + 2Pb.$$

419. Lead, when freshly cut, is a bluish gray metal, at first lustrous, but soon becoming oxidized. It is very malleable, but of inferior ductility and tenacity; so soft as to leave a streak when rubbed upon paper, and melts at 325° C. Its molten surface, when exposed to the air, rapidly oxidizes to *litharge*, PbO; and, by longer heating, to *red lead*, Pb_3O_4 or $2PbO, PbO_2$.

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* The scale is arbitrary and differs with each instrument.

Exp. 194.—Heat dry tartrate of lead in a hard glass tube until the tartaric acid has been decomposed; then cork the tube tightly, and allow it to cool. It contains a mixture of carbon and finely divided lead (*lead pyrophorous*). On pouring this out, it will take fire and burn to litharge.

Hydrochloric and sulphuric acids exert only a surface action upon lead. Its best solvent is nitric acid, somewhat diluted. It is also corroded by acetic acid vapors in the presence of air and moisture. The acetate and nitrate are readily soluble in water, and may be used in forming the insoluble compounds of lead.

420. Lead nitrate, $Pb(NO_3)_2$, crystallizes in octahedra. It is decomposed at a low red heat into oxygen, nitric peroxide, and litharge. Common litharge is an impure, yellow protoxide, obtained in large quantities by the cupellation of silver. Heated for some time below its point of fusion (about 400° C.), it oxidizes further and forms red lead. This oxide, which is sometimes used as a paint, is decomposed by nitric acid,

$$Pb_3O_4 + 2HNO_3 = PbNO_3 + H_2O + PbO_2,$$

yielding lead nitrate, water, and lead dioxide (PbO_2), the last a brown powder which is capable of forming salts with both acids and bases. Like many other peroxides, when treated with hydrochloric acid, it evolves chlorine and forms a chloride.

421. Lead chloride, $PbCl_2$, is soluble in 33 parts of water, and forms as a white crystalline precipitate when hydrochloric acid is added to a strong solution of any lead salt.

422. Lead carbonate, $PbCO_3$, is formed as a white precipitate on adding ammonium carbonate to a solution of any lead salt.

The commercial "white lead" is prepared on a large scale by (1) exposing plates of lead in earthen jars to the fumes of vinegar, whereby it is converted into a basic acetate; (2) then burying them in large heaps of tan-bark. This slowly decays, evolving carbonic anhydride, which converts the acetate into a basic carbonate, and (3) sets free the acetic acid to act upon fresh portions of the lead.

White lead has greater opacity, or "body," than the precipitated carbonate, and, when ground with linseed oil, forms the basis of ordinary white paints.

423. Lead sulphide, PbS, occurs native as galena, and may be formed artificially by passing sulphuretted hydrogen through any solution of lead salts. This is a black, amorphous powder, soluble in nitric acid with liberation of sulphur.

424. The soluble lead salts are all poisonous; and, as lead pipes are often used to convey water, it is necessary to consider the action of water upon lead. (1) Pure water free from air does not act upon lead. (2) If the water contains air, the lead oxidizes, forming a slightly soluble hydrate. (3) If, in addition, the water contains chlorides, nitrates, nitrites, or decomposing organic matters, the oxide formed is dissolved, and the water may be seriously contaminated with poisonous lead salts.

On the other hand, (4) if the water contains phosphates, sulphates, and especially carbonates, the hydrate will be changed to an insoluble salt, which protects the lead from further action. Such waters are generally innocuous; but (5) it must be borne in mind that the lead carbonate is slightly soluble in water containing free carbonic anhydride. Hence, (6) when drinking waters are conveyed through leaden pipes, it is safe to use them only when enough has run through to guaranty that they are uncontaminated with lead.

The antidotes for lead poisoning are the soluble sulphates, as

Epsom salts. Weak sulphuric acid is recommended as a prophylactic for workmen engaged in the manufacture of its compounds.

425. The alloys of lead are numerous. Type metal contains about 20 per cent of antimony, and is distinguished not only for its great hardness, but for the sharp casts which it gives, owing to its expansion at the moment of solidification. Soft solder, which melts at 186° C., is an alloy of nearly equal parts of lead and tin. Shot is lead hardened by about two per cent of arsenic.

426. Tests for lead. Lead resembles the metals of the calcium group in the fact that alkaline carbonates, phosphates, and sulphates, when added to solutions of its salts, produce insoluble precipitates. It differs from them in the stability of the metal, its high specific gravity, by the ready reducibility of its compounds, and by the following reactions.

All lead compounds, when mixed with dry sodium carbonate, are readily reduced before the blowpipe, and yield a malleable metallic bead. This bead, dissolved in nitric acid or any lead salt in solution, yields—

(1) With sulphuretted hydrogen or ammonium sulphide, a black lead sulphide, insoluble in dilute acids;

(2) With hydrochloric acid, a white precipitate soluble in a large excess of boiling water;

(3) With potassium iodide or potassium chromate in neutral solutions, a yellow precipitate.

THE MAGNESIUM GROUP.

427. Magnesium, zinc, and cadmium have many properties in common, and yet present marked differences. They are malleable and somewhat ductile metals which remain unaltered in dry air; but, on being heated, volatilize at high temperatures; and, in the presence of oxygen, burn, forming bulky anhydrous oxides.

These oxides are nearly insoluble in water, but readily combine with acids, forming salts which, in most cases, are isomorphous. Their basic power diminishes with an increase in atomic weights. Magnesium is the most electro-positive of this group. It decomposes boiling water rapidly, while zinc and cadmium act slowly.

On the other hand, magnesium sulphide is decomposed by water; zinc sulphide is soluble in dilute acids (excepting acetic); and cadmium sulphide is insoluble in dilute acids.

It needs also to be remarked that magnesium is related to lithium through the insolubility of its carbonate and phosphate, and to calcium through the isomorphism of their carbonates. All the metals of this group differ from those of the calcium group in the fact that their sulphates are soluble in water.

MAGNESIUM.

428. **Magnesium occurs** in nature as a carbonate (magnesite). Usually this carbonate is associated with lime, as dolomite ($MgCO_3 + CaCO_3$), or is found in enormous masses as magnesian limestone. It is also found as a silicate in talc, serpentine, and meerschaum. Its soluble salts are widely distributed in mineral waters.

Carnallite is a double chloride of magnesium and potassium, found in large quantities at Stassfurth.

429. **The metal magnesium** is obtained by fusing its chloride with sodium: $MgCl_2 + 2Na = 2NaCl + Mg$. It is a silver-white metal, which burns in the air with a white flame of dazzling brilliancy. This flame contains enough of the actinic rays to render it serviceable as an artificial light in photography.

430. **Magnesium oxide,** MgO (*calcined magnesia*), is formed when magnesium is burned in the air, but is

generally prepared by roasting the carbonate. It is a white, bulky, infusible powder, almost insoluble in water, and yet capable, when moistened, of bluing red litmus, forming magnesium hydrate. It gradually changes in the air to magnesium carbonate.

431. Magnesium carbonate, $MgCO_3$. The *magnesia alba* of the druggist is a mixture of magnesium carbonate and magnesium hydrate. It is prepared by adding sodium carbonate to a boiling solution of a magnesium salt, and washing the resulting precipitate. Both the oxide and carbonate are used in medicine as antacids.

432. Magnesium chloride, $MgCl_2$, is formed when hydrochloric acid is added to either of the preceding compounds. Like calcium chloride, it crystallizes with $6H_2O$, and is deliquescent. It can not be deprived of its water of crystallization without decomposition. The anhydrous salt is prepared by igniting the double chloride of magnesium and ammonium: $MgCl_2 + NH_4Cl + 6H_2O$. This first loses its water of crystallization; then the ammonium chloride and the anhydrous magnesium chloride remain.

433. Magnesium sulphate, $MgSO_4 + 7H_2O$ (*Epsom salts*), is a common constituent of mineral waters. It is prepared in considerable quantities from the "bittern" of sea waters, which remains after the sodium chloride has crystallized out; and also from the native carbonate, by treating either with sulphuric acid. It is a very soluble salt, but crystallizes from strong solutions in monoclinic prisms containing seven molecules of water. Six of these molecules are easily driven off by heat, but the seventh is retained even at 200° C. This last atom is the "water of constitution," and may be replaced by various sulphates of other metals, giving rise to double salts with six molecules of water; as,

$$MgSO_4 + K_2SO_4 + 6H_2O.$$

434. All the soluble salts of magnesia have an unpleasant, bitter taste, but many of them are used in medicine as cathartics. All the compounds of magnesia show a strong tendency to combine with the salts of ammonia, and form double salts which are easily soluble in water. Hence, the addition of ammonium salts will very generally hinder the precipitation of magnesium by the ordinary reagents. An exception to this is found in magnesium phosphate.

435. Magnesium phosphate, $MgHPO_4 + 7H_2O$, forms when sodium di-phosphate is added to a magnesium salt. If an ammonium salt is present, a difficultly soluble precipitate of the formula $MgNH_4PO_4 + 6H_2O$ crystallizes out. When this salt is dried and then ignited, it first loses its water, then its ammonia, and becomes changed to magnesium pyrophosphate:

$$2(Mg, NH_4, PO_4 + 6H_2O) = 13H_2O + 2NH_3 + Mg_2P_2O_7.$$

This is the form in which magnesia is generally estimated in quantitative analysis.

ZINC.

436. Zinc occurs in nature chiefly as a sulphide (blende), or as a carbonate (Smithsonite). It also occurs as an oxide (red zinc ore), and as a silicate (calamine).

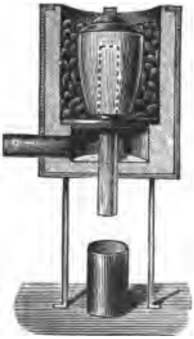


FIG. 90.

In preparing the metal, (1) the ores are roasted in air, whereby they are converted to zinc oxide. (2) This oxide is then mixed with powdered coke and heated in earthen crucibles. At white heat the metal is reduced, and, volatilizing, is condensed in suitable receivers: $ZnO + C = CO + Zn$.

437. Zinc is a bluish-white metal.

It is quite malleable between 100° C. and 150° C., and between these temperatures is readily rolled into sheets. Very curiously, it is brittle both below and above these temperatures, and, in thick plates, breaks with a crystalline fracture. When exposed to the air, zinc soon tarnishes, forming a closely adhering film of oxide, which prevents it from further change. This property is utilized in the so-called galvanized iron, which is iron coated with zinc, to prevent the iron from rusting. Zinc is easily soluble in most acids and in boiling caustic alkalies, with evolution of hydrogen.

$$(1)\quad H_2SO_4 + Zn = ZnSO_4 + \hat{H}_2.$$

$$(2)\quad 2KHO + Zn = K_2ZnO_2 + \hat{H}_2.$$

In both these cases the action is accelerated by the presence of another metal, as a coil of platinum wire.

Zinc is used as the electro-positive metal in most galvanic batteries, and in the form of sheets for roofing and other purposes.

438. Zinc chloride, $ZnCl_2$, is formed when zinc is dissolved in hydrochloric acid. The solution is used as a disinfectant and in soldering. On evaporating the solution to dryness, a white, deliquescent salt is obtained, which absorbs water greedily, and is sometimes used in surgery as a caustic.

439. Zinc hydrate, $Zn(HO)_2$, is formed when any alkali is cautiously added to a solution of a zinc salt. It is easily soluble in an excess of the precipitant. When dried, it is readily decomposed by heat into *zinc oxide*, ZnO. This body is usually prepared by burning zinc in a current of air. It is a light powder, yellow when hot and white when cold, and extensively used as a paint, under the name of "zinc white."

440. Zinc sulphate, $ZnSO_4 + 7H_2O$, may be obtained by evaporating a solution of zinc in sulphuric acid, as colorless prisms, isomorphous with magnesium sulphate, which it strongly resembles. It also forms double salts with $6H_2O$; as, $ZnSO_4 + K_2SO_4 + 6H_2O$. It is used in medicine, and produces vomiting when swallowed in even moderate doses.

441. Zinc carbonate occurs native. The precipitate which forms when an alkaline carbonate is added to a zinc solution always contains zinc hydrate, and is a basic carbonate, although its composition varies with the mode of preparation, *e. g.*, $2ZnCO_3 + 3Zn(HO)_2$.

442. Zinc sulphide, ZnS, is formed when zinc salts are decomposed by ammonium sulphide. It is easily soluble in dilute acids (excepting acetic), and is readily oxidized when heated in air. It is the only insoluble white sulphide formed in the wet way, and hence is a characteristic test for zinc.

443. Zinc alloys are numerous and important. Brass contains about one part of zinc to two of copper. German silver contains, in addition, one part of nickel. Many varieties of bronze also contain zinc.

CADMIUM.

444. Cadmium is found in small quantities, associated with zinc ores. Being more volatile than zinc, it is obtained from the first portions of the distillate in zinc smelting.

It is a soft, white, easily fusible, and volatile metal. It burns somewhat readily in air, forming a brown oxide, CdO. The metal is used to form alloys, which fuse at very low temperatures. An alloy 8 parts of lead, 15 of bismuth, 4 of tin, and 3 of cadmium, melts at 60° C. (Wood's metal).

Its sulphide is used in water-colors as a yellow pigment. Cadmium iodide is used by photographers.

Tests for the Magnesium Group.

445. In analytical chemistry, these metals are placed in three different groups, because of the behavior of their sulphides.

I. (*a*) In acid solutions, sulphuretted hydrogen precipitates cadmium only as a characteristic, yellow, amorphous powder, insoluble in dilute acids. (*b*) In neutral or alkaline solutions it precipitates white zinc sulphide, which is soluble in all dilute acids, except acetic. (*c*) Magnesium does not form a sulphide in the wet way. If a solution containing these three elements has been treated successively with sulphuretted hydrogen, and ammonium sulphide is mixed with sodium di-phosphate, white $MgNH_4PO_4$ precipitates.

II. The fixed alkalies precipitate all these elements as white hydrates. Zinc hydrate alone is soluble in potash and soda.

III. The alkaline carbonates produce white basic carbonates. The presence of ammoniacal salts either hinders (Cd) or prevents (Mg, Zn) the formation of this precipitate.

IV. Heated before the blowpipe on charcoal, (*a*) magnesium oxide becomes intensely luminous; the residue, moistened with cobalt solution and reheated, yields a pink mass. (*b*) Zinc oxide becomes yellow while hot, and again white on cooling. Moistened with cobalt solution and reheated, it forms a green mass. (*c*) Cadmium oxide, when anhydrous, is a brown powder.

446. Rare dyad metals. To this group are usually referred a number of rare metals which have not been thoroughly classified. Some of these are, perhaps, triads, as their oxides resemble alumina. They have been found only in a few rare minerals, principally obtained in the Scandinavian peninsula.

They are glucinum; thorinum, yttrium, and erbium; lanthanum and didymium; and cerium.

Cerium only has received any practical application. Some of its salts have been used in medicine in various dyspeptic conditions of the stomach.

447. Mercury and copper are metals not easily classified. They form two series of compounds: (1) *ic* salts, in which they act as dyad elements, as $HgCl_2$, mercuric chloride, and $CuCl_2$, cupric chloride; (2) *ous* salts, in which they are apparently monad elements, as HgCl, mercurous chloride, and CuCl, cuprous chloride.

Theoretically, it is better to consider that these elements are always divalent, and that their *ous* salts contain a double atom of the metal whose affinities partially satisfy each other. Thus the theoretical formula of mercurous chloride is Hg_2Cl_2, and of cuprous chloride, Cu_2Cl_2. These may be represented graphically thus:

$$\begin{array}{l} \text{Hg—Cl} \\ \;| \\ \text{Hg—Cl} \end{array} \qquad \begin{array}{l} \text{Cu—Cl} \\ \;| \\ \text{Cu—Cl} \end{array}$$

The *ous* salts of both resemble those of silver; the *ic* salts resemble those of the dyad group.

MERCURY.

448. Mercury is not widely distributed. It occurs, however, in considerable quantities in a few localities, of which the best known are Idria, in Austria; Almaden, in Spain; and New Almaden, in California. The metal sometimes occurs native, but its principal ore is the sulphide HgS (*cinnabar*), from which it is generally extracted.

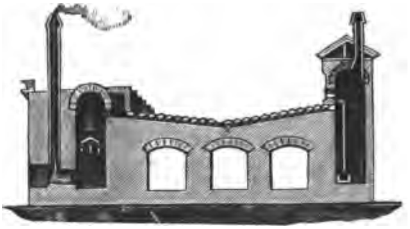


FIG. 91.

The process is very simple. The sulphide heated in air easily decomposes, yielding sulphurous anhydride and mercury:

$$HgS + O_2 = SO_2 + Hg.$$

Sometimes lime is added. The mercury volatilizes and is conducted through earthen pipes, called aludels. The mercury which escapes condensation in the aludels is condensed in large brick chambers.

449. Mercury is the only metal which is liquid at ordinary temperatures. It is largely used in the construction of barometers, and in apparatus for the measurement of gases. It is the most available liquid in the construction of thermometers, because it expands regularly, on being heated, from 0° C. to 100° C. It is solid at —40° C.; volatilizes at all temperatures above 10° C.; and boils at 360° C., yielding a colorless vapor 100 times as dense as hydrogen. It possesses a bright, grayish-white luster, which is scarcely tarnished on exposure to the air. Heated for a long time in air, it forms the red oxide, HgO. It enters into combination with chlorine, bromine, iodine, and sulphur at ordinary temperatures. It decomposes strong boiling sulphuric acid, forming mercuric sulphate; but its best solvent is nitric acid. With this it forms mercurous nitrate, $Hg_2(NO_3)_2$, and mercuric nitrate, $Hg(NO_3)_2$, besides a large number of basic salts.

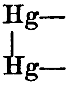
450. Mercury forms two series of compounds as unlike in their properties as if they had been formed from two different elements. The first series, typified by corrosive sublimate, $HgCl_2$, is the *mercuric* series; the other series, which is typified by calomel, $HgCl$ or Hg_2Cl_2, is the *mercurous* series.

The mercurous compounds are frequently written with half their molecular formulæ; thus, mercurous chloride, or calomel, is represented either by Hg_2Cl_2 or by $HgCl$.

451. The mercurous salts are readily converted by oxidizing agents to mercuric compounds; and the mercuric compounds as easily converted by reducing agents to mercurous compounds.

All compounds of mercury, and even the vapor of mercury, have a decided action when taken in any way into the human system; producing, in excess, a disagreeable and sometimes dangerous salivation. It is, however, curious to note that the mercuric compounds are more energetic in their action, and are deadly poisons. The mercurous compounds are milder, and are more frequently used in medicine.

MERCUROUS SERIES,



$$\begin{array}{l}Hg—\\ |\\ Hg—\end{array}$$

452. Mercurous nitrate, $Hg_2(NO_3)_2$, forms when mercury is digested in an excess of cold, dilute, nitric acid. Basic salts form when the mercury is in excess, and mercuric salts, in warm solutions or in strong nitric acid. Mercurous nitrate forms colorless tables, partially decomposed by water, but soluble in water acidified by nitric acid. It is advisable always to add to this solution a little metallic mercury, to prevent the formation of mercuric salts.

453. Mercurous oxide, Hg_2O, is a black, amorphous powder, obtained by adding sodium hydrate to a solution of mercurous nitrate. It is decomposed by heat and light into Hg and HgO.

454. Mercurous chloride, Hg_2Cl_2, or calomel, is a white, amorphous powder, insoluble in water and dilute acids, which may be obtained by adding hydrochloric acid to mercurous nitrate.

Commercially, it is made by subliming (1) a mixture of mercuric chloride and mercury, or (2) a mixture of mercuric sulphate, mercury, and common salt: $HgSO_4 + Hg + 2NaCl = Na_2SO_4 + Hg_2Cl_2$. The vapor is condensed in large chambers, and is then ground to a powder and washed with water. Sodium hydrate decomposes it, yielding black mercurous oxide.

455. Mercurous iodide, Hg_2I_2, is a greenish yellow powder, obtained by mixing solutions of mercurous nitrate and potassium iodide. It is insoluble in alcohol.

MERCURIC SERIES, Hg″.

456. Mercuric oxide, HgO. This has two forms: (1) the red oxide, which is prepared by heating mercury for several days in air at about 315° C.; and (2) a yellow oxide, by adding potassium hydrate to a solution of mercuric salts. The yellow oxide is more susceptible of chemical change, which is perhaps due to the more finely divided state of the precipitated oxide. Either of these forms, on being heated, takes on a darker color, and, at 400° C., decomposes into oxygen and mercury. The residue, if any, becomes red on cooling.

457. Mercuric nitrate, $Hg(NO_3)_2$, is best prepared by dissolving mercuric oxide in an excess of nitric acid. It crystallizes in small needles, which are decomposed by heat, leaving the red oxide.

458. Mercuric chloride, $HgCl_2$ (*corrosive sublimate*). This important salt is obtained usually by subliming a mixture of mercuric sulphate with common salt:

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2;$$

for laboratory purposes, by dissolving mercury in aqua regia. It is easily soluble in water and in alcohol, and, on crystallizing, forms rhombohedral prisms which melt at 270° C., and sublime unchanged at 300° C. Its solution has a sharp, metallic taste, and is an active poison. It coagulates albumin, forming with it insoluble "albuminates." Hence, it has been largely used as an antiseptic in preserving animal and vegetable tissues from decay; and hence, also, albumin is an excellent antidote in cases of poisoning by corrosive sublimate.

459. Mercuric iodide, HgI_2, is formed when potassium iodide is added to a solution of mercuric salts. It is first salmon-colored, but changes to a beautiful red precipitate, which is insoluble in water. An excess of either

reagent must be avoided, because very soluble double salts are formed, such as HgI_2KI or HgI_22HgCl_2. If the red iodide is heated, it sublimes in yellow, prismatic cystals, which slowly revert to red octahedra if left untouched, and immediately when rubbed with any hard substance. It therefore exhibits a remarkable example of dimorphism.

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464. The preparation of copper from its native form or from its oxygen compounds requires merely the

smelting of the ore with coal. The reduction of copper from the sulphide is a more complex process.

(1) The ore is first roasted in a reverbatory furnace (Fig. 80), whereby certain constituents (As, Sb, S) are volatilized, and others oxidized (FeS_2 to Fe_2O_3). (2) This product is roasted with a mixture of coal and silicates, to produce a soluble *slag* with the iron, while the copper accumulates as a nearly pure sub-sulphide (Cu_2S). (3) When the iron has been removed by a succession of these operations, the heat is raised and a portion of the copper is oxidized and reacts upon the remaining sub-sulphide ($2CuO + Cu_2S = SO_2 + 4Cu$), yielding metallic copper. (4) The final stage of the process consists in stirring up the melted mass with a long stick of green wood, which reduces the last portions of the oxide. The metal is then drawn off and cast into ingots.

465. Copper is a reddish metal, very malleable, ductile, and tenacious, and is one of the best conductors of heat and electricity. It preserves its brilliant luster unchanged in dry air, unless heated, when it oxidizes rapidly, forming a many-colored film, which finally changes to scales of the black oxide. In moist air it becomes dull looking, and slowly forms a crust of green basic carbonate. This change takes place more rapidly in the presence of acid vapors, or when the copper is moistened with ammonia or with solutions of chlorides.

466. It is a dyad which differs from all those previously studied in its high melting point (1200° C.), and in the fact that it is only slightly volatile, even at very high temperatures. It resembles mercury in some of its properties: (1) in that it is hardly attacked by hydrochloric or sulphuric acid, except when heated, but readily dissolves in dilute nitric acid; (2) by forming ammonium compounds in which the copper apparently replaces a part of the hydrogen of the ammonium, as $2NH_3, CuCl_2$; and (3) in forming two series of salts—the cuprous, typified by cuprous chloride (Cu_2Cl_2), and the cupric, typified by cupric chloride ($CuCl_2$). The latter series is by far the most abundant and important of the copper compounds.

467. Cuprous chloride, Cu_2Cl_2, is best made by digesting for some time a mixture of copper filings and cupric oxide in hydrochloric acid. The salt is soluble in hydrochloric acid; but, when the solution is poured into a large quantity of water, it separates out as a white crystalline powder.

468. Cuprous oxide, Cu_2O, is obtained when a solution containing cupric sulphate, grape sugar, and an excess of sodium hydrate, is warmed. Generally, a yellow cuprous hydrate, Cu_2O, H_2O, first separates out; but, on longer boiling, anhydrous red cuprous oxide is formed. This reaction is facilitated by a considerable addition of tartaric acid. The red oxide is used to impart a beautiful ruby color to glass.

Most oxy-acids decompose this oxide, precipitating metallic copper and forming cupric salts.

469. Cupric oxide, CuO, may be prepared by roasting copper in air or by igniting the nitrate. When sodium hydrate is added in excess to a solution of a cupric salt, a pale blue precipitate forms, which is cupric hydrate, $Cu(HO)_2$; but, upon heating the mixture, the black anhydrous oxide forms, even in the presence of water. It is easily reduced, especially in the presence of hydrocarbons, for which reason it is extensively used as an oxidizing agent in organic analyses.

Combined with oxy-acids, it forms a large series of salts, which are all white when anhydrous, and blue or greenish when hydrated.

470. The native sulphide, CuS, has already been mentioned as one of the chief sources of copper. It is formed artificially as a black precipitate when sulphuretted hydrogen is added to cupric solutions. It is readily oxidizable in air, forming cupric sulphate.

471. Cupric sulphate, $CuSO_4 + 5H_2O$ (*blue vitriol*), is the most important salt. It is obtained on boiling copper in strong sulphuric acid, as blue triclinic prisms:

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

These crystals are changed to a white anhydrous powder at about 200° C., which absorb water greedily, and again become blue. Hence, it is used to remove the last portions of water from alcohols, ethers, etc. Although it contains but $5H_2O$, it forms with alkaline sulphates double salts containing $6H_2O$, and therefore analogous, as they are isomorphous with magnesium double sulphates; *e. g.*, $K_2, Cu(SO_4)_2 + 6H_2O$. With an excess of aqua ammonia, it forms an exceedingly soluble blue compound ($4NH_3$, H_2O, $CuSO_4$), which, upon being dried and heated to 150° C., becomes cupric-ammonium sulphate, $2NH_3, CuSO_4$.

472. Cupric nitrate, $Cu(NO_3)_2$, is made by dissolving copper in nitric acid. On evaporating, bright blue crystals form, which are very deliquescent and easily decomposed by heat, leaving cupric oxide.

473. Numerous carbonates of copper occur in nature. The most prized of these is malachite, which takes a high polish and is used for ornaments. A similar compound forms when sodium carbonate is added to a hot solution of a cupric salt, $CuCO_3 + Cu(HO)_2$.

474. The uses of copper in the arts are well known; but, perhaps, its alloys are more extensively used than the metal itself. Gun metal, bell metal, bronze, and speculum metal are alloys with tin, containing from 66 to 90 per cent of copper. They are distinguished by great hardness, and a susceptibility of taking on a high polish. Copper is also a constituent of brass, German silver, most alloys of silver, and of "red" gold.

The sulphate of copper is largely used in galvanic batteries and in electrotyping. Some of the salts of copper are valuable pigments. Brunswick green is an oxy-chloride. Scheele's, or Paris, green and Schweinfurt green are arsenites; beautiful greens, but very poisonous. Verdigris is a basic acetate, although this term is often incorrectly applied to the green basic carbonate which forms when copper is exposed to moist air.

It must not be forgotten that all soluble salts of copper are *active poisons.* Too much care can not be taken to keep copper vessels used for cooking perfectly bright and clean, as the presence of oily matters facilitates the solution even of the black oxide. Its proper antidote is the albumen of eggs.

TESTS.—(1) Ammonia, added to any cupric solution, produces at first a greenish blue precipitate which dissolves in excess, forming an azure blue solution. (2) Potassium ferrocyanide gives a dark brown precipitate of cupric ferrocyanide. (3) Sulphuretted hydrogen, or an alkaline sulphide, forms a black precipitate insoluble in dilute acids and slightly soluble in ammonia. (4) A bright slip of iron plunged in an acid solution of copper, even when quite dilute, becomes soon coated with the red metal.

Recapitulation.

Review §§ 400, 401; 427; 447.

These dyad elements may be arranged with the monads Li and Ag into sub-groups, as follows:

I		II		III	
Calcium,	40	(Li. 7)		Copper,	63
Barium,	87.5	Magnesium,	24	(Ag 108)	
Strontium,	137	Zinc,	65	Mercury,	200
Lead,	204	Cadmium,	112	Lead,	207

Their carbonates are insoluble in H_2O, and are decomposed by heat, yielding oxides.

The oxides of the first sub-group resemble those of the alkalies, BaO being the nearest.

The chlorides of the first and second sub-groups are all soluble in water, and most are deliquescent bodies.

The protochlorides of the third sub-group are either insoluble in water or difficultly soluble (Pb in 33 parts).

CHAPTER XIII.

THE TRIAD METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	MELTING POINT, °C.	DISCOVERER.
Indium	In	113.4	7.4	176°	Reich and Richter, 1863.
Gold	Au	197	19.34	1250°	
Thallium	Tl	204	11.8	285°	Crookes, . . . 1861.

475. These metals have few properties in common, beyond the fact that they are triad elements, uniting with three atoms of chlorine to form $InCl_3$, $TlCl_3$, and $AuCl_3$.

Indium and thallium are very rare. The principal interest that attaches to them is derived from the fact that they were recently discovered by the application of the spectrum analysis. The spectrum of indium contains two bright blue bands. It occurs in some ores of zinc, which metal it very much resembles. Thallium is more widely distributed, though in very small quantities. Its principal sources are certain iron and copper pyrites. In its physical properties it resembles lead; but, in its chemical, is more closely allied to the alkalies, forming a caustic hydrate, $TlHO$, and to silver, forming an insoluble white chloride, $TlCl$.

GOLD.

476. Gold is more widely distributed than is generally supposed, being found in many alluvial sands in all parts of the world. Its richest deposits are in California and Australia. It is generally found native, but is frequently associated with ores of other metals. It is obtained (1) by simple washing in a stream of water, or (2) by treating the crushed ore with mercury, which dissolves out the gold. The resulting amalgam is distilled, the mercury is recovered for future operations, and the gold which remains is cast into bars.

477. Gold is a yellow metal, of high specific gravity, very malleable and very ductile. When obtained in very thin sheets, it transmits a green light. It is so soft that pieces of pure gold foil may be welded together by pressure, as in dentistry. The gold used in coins or for ornaments is hardened by being alloyed by copper or by silver.

An ancient commercial method of measuring the fineness of gold still obtains: pure gold is reckoned at 24 carats; and the alloys are said to be as many carats fine as they contain parts of gold in 24. Thus, the best jewellers' gold is 18 carats fine, and contains $\frac{18}{24}$ of its weight in gold. One U. S. gold dollar weighs 25.8 grains, and contains 90 per cent of gold (21.6 carats fine). At this rate, pure gold is $20.67 per Troy ounce. British coin is 22 carats fine.

478. Gold is not acted upon by air, by water, or by ordinary acids. It, however, dissolves readily in any liquid which contains free chlorine. Aqua regia is its best solvent, yielding *auric chloride.*

479. Auric chloride, $AuCl_3$, on evaporation forms a red deliquescent mass. With alkaline chlorides it forms yellow, needle-like crystals; as, $NaAuCl_4 + 2\,H_2O$. The commercial chloride has the formula $AuCl_3, HCl$. Heated to about 150° C., it partially decomposes, leaving *aurous chloride,* a white powder insoluble in cold water.

480. Auric oxide, $3H_2O, Au_2O_3$, forms when auric chloride is digested with magnesia. It possesses no basic properties, but rather acts as a weak acid. It dissolves in excess of potassium hydrate, and, on evaporating, yields yellow needles: $K_2O, Au_2O_3 + 3H_2O$.

Aurous oxide, Au_2O, acts as a feeble base. Its only important salt is made by mixing solutions of auric chloride and sodium hyposulphite. It is a double hyposulphite of gold and sodium: $Na_3Au, 2S_2O_3 + 2H_2O$. It is used by photographers in "toning"; and, very curiously, neither ferrous sulphate nor stannous chloride serves to detect gold in its solution.

481. The uses of gold in coinage and in ornaments have been known through all ages of the world. In recent times, it has been largely employed in gilding, especially by the application of galvanism. The gold is usually deposited from a solution of the cyanide, $Au(CN)_3$, and may be obtained in any required thickness. Gold, in its finely divided state, as in the purple of Cassius, is used to impart a ruby color to glass, and for gilding porcelain.

TESTS.—(1) All gold compounds are readily reduced to metallic gold by heating.

(2) Gold is also easily reduced in solutions not containing free nitric acid by ferrous sulphate, by oxalic acid, and by many other reducing agents in the form of a brown powder.

(3) Stannous chloride produces a purple precipitate (purple of Cassius), which is, perhaps, Au_2O, SnO, SnO_2.

CHAPTER XIV.

THE TETRAD METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	DISCOVERER.
Osmium	Os	199	21.4	Tennant, 1803.
Ruthenium	Ru	104.4	11.4	Klaus, 1844.
Iridium	Ir	198	21.1	Tennant, 1803.
Rhodium	Rh	104.4	12.	Wollaston, 1804.
Platinum	Pt	197.5	21.5	Wood, 1741.
Palladium	Pd	106.6	11.8	Wollaston, 1803.
Davyum	Da	150?	9.4	S. Kern, 1877.
TRIAD AND MONAD METALS.				
Gold	Au	197	19.3	Known from earliest times.
Silver	Ag	108	10.5	

482. These metals are popularly classed together as the "noble metals." They possess many properties in common, viz: a remarkable power of resisting oxidation and of retaining their luster unchanged in air; a high fusing point; large atomic weights; and high specific gravities. It will be observed that in the table they are arranged in pairs. The two members of each more strongly resemble each other than they do the other members of the group, although their atomic weights and specific gravities bear nearly the proportion of 1 : 2.

Gold and silver, which we have already studied, agree in forming an insoluble monad chloride, and soluble double salts with the alkaline chlorides. They differ in their fusing points, in specific gravity, and in the power of resisting oxidation. Somewhat similar relations and differences are found in the other pairs of the group, especially between platinum and palladium; but we must not attempt to form a strict parallelism.

483. The first six metals of the table are tetrad metals, known as the platinum group. Though sometimes found native, these more frequently occur as alloys containing from two to four of the metals; as, for example, palladium is generally found with platinum. Iridium, rhodium, and osmium also occur with platinum; while iridosmine (a very hard mineral used for the points of gold pens) generally consists of iridium, osmium, rhodium, and ruthenium. Davyum, the last discovered of the elements, is found in small quantities in ores of platinum.

484. Osmium and ruthenium are white, brittle metals, nearly or quite infusible in the oxy-hydrogen blowpipe. Nevertheless, osmium is somewhat volatile, and both differ from the other metals of this group in combining with oxygen in the air at high temperatures. Their highest oxides are OsO_4, RuO_4, which are the only tetroxides known, and are neutral bodies of offensive odor, combining neither with bases nor acids. Their tri-oxides act as acids. They form, in all, five oxides; as, OsO, Os_2O_3, OsO_2, OsO_3, OsO_4; and three chlorides; as, $OsCl_2$, Os_2Cl_6, and $OsCl_4$. These, however, are not of sufficient importance to warrant further notice.

485. Iridium and rhodium are grayish-white metals, hard and brittle, and with difficulty fused in the oxy-hydrogen flame. When pure, they are not soluble, even in aqua regia, but may be oxidized by fusion with niter. Iridium forms three chlorides: $IrCl_2$, Ir_2Cl_6, and $IrCl_4$. Only one chloride of rhodium is known—Rh_2Cl_6; but an oxide, RhO_2, is known.

486. Platinum and palladium are the most abundant of the members of this group. They are also more nearly related, being both brilliant white metals, fusible only in the oxy-hydrogen flame, quite malleable and ductile, and possessing considerable tenacity. In all these respects palladium is the inferior metal, but it surpasses platinum in hardness.

Both form two chlorides: $PlCl_2$, $PlCl_4$, and $PdCl_2$, $PdCl_4$, and the corresponding oxides; that is, they act both as bivalent and quadrivalent elements.

487. Palladium is the only metal of the group which is soluble in HCl, H_2SO_4, and in HNO_3. The nitrate, $Pd(NO_3)_2$, is used for the quantitative determination of iodine, forming, when added to solutions of iodides, a black precipitate of PdI_2.

488. The metal palladium possesses the curious faculty of absorbing, or "occluding," about 900 times its volume of hydrogen. This product is sometimes regarded as an alloy of palladium with hydrogen. It is a stronger reducing agent than hydrogen itself, easily reducing $HgCl_2$ to Hg_2Cl_2, and finally to Hg.

489. The metal platinum, in a state of fine division (spongy platinum or platinum black), absorbs more than 200 times its volume of oxygen, and then acts as a strong oxidizing agent, being capable of converting alcohol to acetic acid, and of setting on fire a stream of hydrogen.

490. Platinum tetrachloride, $PtCl_4$, is the only important salt of platinum. It is obtained as a yellow, extremely deliquescent mass when platinum is dissolved in aqua regia. Its principal use is to form double chlorides with alkaline chlorides. All of these, except that with sodium, are difficultly soluble in water and alcohol. Hence, platinum tetrachloride is a valuable reagent in the quantitative determination of the alkalies, except sodium.

491. The double chloride, $PtCl_4, 2NH_4Cl$, when heated to redness, is entirely decomposed, yielding the "spongy platinum" above referred to. Platinum black is platinum in a still finer state of division, obtainable by heating a mixture of solutions of sugar, sodium carbonate, and platinum tetrachloride. It is used as a coating on the silver plate in Smee's battery.

492. Platinum is the only metal of this group which has received any extensive applications in the arts. It is especially valuable for crucibles, sulphuric acid stills, and in the wires used for electric fuses. It was for a time used in Russia for coins, but was not found convenient.

Tests.—(1) All dry salts of the platinum group are reduced by heat alone, frequently to spongy masses; all infusible, except by the oxy-hydrogen blowpipe.

(2) All solutions of the salts of these metals are precipitated as brown or black sulphides by H_2S. Of these the sulphides of platinum and iridium are soluble in ammonium sulphide.

Recapitulation.

The noble metals are difficultly fusible, and are not easily acted upon by acids.

$PtCl_4$ forms difficultly soluble double salts with most of the alkaline chlorides.

Ag, Au, and Pt alone find extensive employment in the arts.

CHAPTER XV.

THE HEXAD GROUP OF METALS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	DISCOVERER.	
Nickel	Ni	58.7	8.82	Cronstedt,	1751.
Cobalt	Co	59	8.95	Brandt,	1733.
Iron	Fe	56	7.84		
Manganese	Mn	55	8	Scheele,	1774.
Chromium	Cr	52.2	6.81	Vauquelin,	1797.
Aluminium	Al	27.4	2.6	Woehler,	1828.
Gallium	Ga	69.9	5.93	Lecoq de Boisbaudran,	1875.
Molybdenum	Mo	92	8.62	Hielm,	1782.
Tungsten	W	184	17.6	d'Elhujar,	1781.
Uranium	U	240.	18.3	Klaproth,	1789.

493. Molybdenum and tungsten resemble each other, but differ in most respects from the remaining metals given in the table. They are rare elements imperfectly studied, and are probably hexad, as shown by the chlorides, MoO_2Cl_2, WCl_6, and the anhydrides, MoO_3, WO_3. They also form a variety of complex products. The only compound of importance is ammonium molybdate, $(NH_4)_2O, MoO_3$, which is used in precipitating phosphoric and arsenic acids from acid solutions.

494. Uranium is a rare metal which, in its analytical reactions, somewhat resembles iron. Its nitrate has the formula $UO_2(NO_3)_2$, and is a yellow, crystalline salt, easily soluble in water. When heated, it leaves a residue of yellow U_2O_3, which, when further ignited, becomes brown UO_2. When treated in solution with sodium hydrate, it precipitates as uranium hydrate, $UO_2(OH)_2$, a yellow body capable of acting both as an acid and as a base. The group $(UO_2)''$ is called *uranyl*, a diatomic radical, which is an unusual form. This radical appears in many of its compounds, as UO_2Cl_2, and in its most usual mineral, $UO_2, 2\,UO_3$. Uranium is used in the determination of phosphorus by volumetric analysis, forming in solutions of phosphoric acid salts an amorphous yellow precipitate, insoluble in acetic acid, of the formula $(UO_2)''HPO_4 + 4\,H_2O$. The oxides of uranium are used in preparing a canary-yellow glass.

495. The other elements given in the table are frequently classed together as the "iron group." Those that are arranged in pairs often show striking resemblances; but it can not be said that the group as a whole is so definitely characterized as several of those which have been already studied.

The one particular in which they all agree is in the formation of a sesqui-oxide, R_2O_3; and all except nickel have the corresponding hexachloride, R_2Cl_6. If we admit the double atom R_2, these elements are tetratomic or hexatomic,

$$\text{as, } \begin{array}{l}Fe\equiv Cl_3\\ | \\ Fe\equiv Cl_3\end{array} \text{ or } \begin{array}{l}Fe\equiv Cl_3\\ ||| \\ Fe\equiv Cl_3\end{array} \text{ and } \begin{array}{l}Al\equiv Cl_3\\ | \\ Al\equiv Cl_3\end{array} \text{ or } \begin{array}{l}Al\equiv Cl_3\\ ||| \\ Al\equiv Cl_3\end{array},$$

in these compounds. Admitting only the single atom, and writing the formula $AlCl_3$, they are apparently triad. Some chemists prefer to reckon aluminium only as a triad, since it forms only this series of compounds. Nevertheless, it is closely related to chromium and to iron. Chromium forms an undoubted hexad, CrF_6; and probably in the higher oxides, CrO_3, FeO_3, MnO_3, chromium, iron, and manganese are hexads. With the exception of aluminium, all the members of the group also act as dyads; as, $NiCl_2$, $FeCl_2$. Nickel forms only this series of salts, and the dyad salts of the other elements are quite stable. The dyad oxides are all strong bases, forming salts which resemble those of zinc and magnesium, with which, also, they are isomorphous, and, like them, form double sulphates with the alkalies; as, $K_2Fe(SO_4)_2 + 6H_2O$.

496. The tetrad oxides, Fe_2O_3, Cr_2O_3, Al_2O_3, Mn_2O_3, are weak bases, forming with alkalies double sulphates which are alums; as, $Al_2O_3, 3SO_3 + K_2O, SO_3 + 24H_2O$ or $AlK(SO_4)_2 + 12H_2O$. The sesquioxide of aluminium acts also as an acid, forming with the alkalies aluminates; as, K_2O, Al_2O_3, or $KAlO_2$.

The hexad oxides are acid anhydrides, forming salts like K_2O, CrO_3 and K_2O, MnO_3.

497. It will be noticed that in the table on page 192 manganese is placed among the heptad elements. Manganese forms a fluoride MnF_7, and is probably septivalent in the permanganates; as, K_2O, Mn_2O_7 or $OK-Mn\equiv O_3$.

NICKEL AND COBALT.

498. These elements are strikingly similar. They generally occur together in nature, being found native in meteoric iron, but more frequently as sulphides or arsenides, associated with other metals. The process of extracting the nickel and cobalt from these ores is very complicated. From the oxides, the metals are obtained by roasting with charcoal at white heat; or from the oxalates, by simple ignition. The oxalic acid decomposes, yielding carbonic oxide, which reduces the remaining oxide. Cobalt is the less abundant, and is not produced in the metallic state on a large scale. Nickel has quite an extensive use in certain alloys, as German silver, and in small coins; and recently has been employed in nickel-plating, to protect steel instruments from rusting.

499. **Both metals resemble iron** in their physical properties. They are white, hard, malleable, and tenacious metals, the tenacity of cobalt even exceeding that of iron; and are also strongly magnetic, but less so than iron. They resist oxidation in moist air, and are not easily soluble in either hydrochloric or sulphuric acids. Their best solvent is nitric acid.

500. **Both form** a stable series of salts, in which they act as divalent metals. The hydrated salts of nickel are generally green, but yellow when anhydrous; those of cobalt are generally rose-red when cold, but on heating, blue, becoming anhydrous.

501. **The most important salt** of nickel is *the sulphate*, $NiSO_4\,7H_2O$, which forms crystals isomorphous with those of magnesium sulphate. It also forms with alkaline sulphates double salts; as, $K_2Ni(SO_4)_2 6H_2O$.

On adding caustic soda to a solution of the sulphate, an apple-green hydrate, NiO, H_2O, precipitates, which is easily soluble in acids. From this may be prepared nickel chloride, $NiCl_2$, by the addition of hydrochloric acid. On adding sodium carbonate or oxalic acid to a moderately concentrated solution of the sulphate, bluish-green precipitates form, which are respectively carbonates or oxalates of nickel.

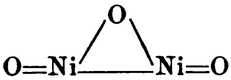
502. **The most important salt** of cobalt is *the nitrate*, $Co(NO_3)_2+6H_2O$, a deliquescent, very soluble, rose-red salt. Its solution treated with sodium hydrate yields CoO, H_2O, which is at first blue and then changes to

rose-red. Either the hydrate or the nitrate, when heated, changes to the brown anhydrous sesqui-oxide Co_2O_3. This is an important agent in blowpipe analysis. It yields, when ignited with various other oxides, residues of characteristic colors, viz: with magnesia, a pink mass; with zinc, a green mass; and with alumina, a blue mass. Still more remarkable is the magnificent blue which it communicates to borax or to alkaline silicates. These reactions have also been used in the arts upon a large scale to produce pigments such as Rinman's green (with ZnO) and Thenard's blue (with Al_2O_3), for imparting a sapphire-blue color to porcelain glaze, and for making blue glass. *Smalt* is blue glass ground to a fine powder and washed.

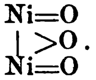
503. Cobaltic nitrite. If to a strong solution containing cobalt, a strong solution of potassium nitrite is added, and then enough acetic acid to liberate the nitrous acid, all the cobalt, upon standing, is precipitated as a difficultly soluble yellow powder (Co_2O_3, $3K_2O$, $5N_2O_3$). Nickel does not form a corresponding salt, and hence this difference in reaction is one of the means used to separate the two elements.

504. Cobaltous chloride, $CoCl_2$. is obtained in red prisms containing $6H_2O$, by dissolving either the oxide or the carbonate in hydrochloric acid. If a drawing is made with its dilute solution upon paper, it is nearly colorless; but, when heated to about 150°, it becomes anhydrous and appears as a bright blue, which again disappears in moist air. This property has led to its use in a so-called chemical hygrometer, and in sympathetic inks.

505. Both nickel and cobalt, when their dyad solutions are mixed with ammonia, yield a hydrate which dissolves in excess of ammonia. The solution contains a double salt of ammonia and the salt of nickel or cobalt used. If, now, chlorine gas be passed into either solution, a black precipitate forms which is the hydrated sesquioxide, $Ni_2O_33H_2O$ or $Co_2O_33H_2O$. The same precipitate forms when an alkaline hypochlorite is added to either hydrate in the presence of free alkali. In these sesquioxides both metals act as tetrads; thus:



or



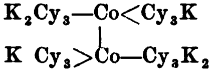
$$\begin{array}{l} \mathrm{Ni{=}O} \\ \mid\!>\mathrm{O}. \\ \mathrm{Ni{=}O} \end{array}$$

Nickel forms no other tetravalent compounds.

506. Cobalt forms, as a tetravalent element, several salts, among which those with ammonia and cyanogen are the best known.

(1) If the solution of cobaltous hydrate in ammonia is exposed to the air, it gradually absorbs oxygen to form cobaltic compounds (of Co_2O_3) with ammonia. These compounds are very numerous and of complex constitution. They may be very generally regarded as ammonium compounds, in which the double atom of cobalt has replaced two or more hydrogen atoms of ammonium. The roseocobaltic chloride has the formula $Co_2Cl_6, 10H_3N + 2H_2O$.

(2) If to a solution of a dyad salt of nickel or of cobalt, potassium cyanide in solution is cautiously added, the cyanides, $NiCy_2$ (greenish) or $CoCy_2$ (brownish), precipitate. Both dissolve in an excess of the potassium cyanide. The nickel double cyanide suffers no further change. Freshly precipitated mercuric oxide precipitates from this solution nickel oxide completely. If, however, the cobaltous double cyanide is exposed to the air, it forms the potassium cobalti-cyanide, from which the cobalt is not precipitated by mercuric oxide nor by ordinary reagents. The cobalt in this is probably tetravalent; thus:



$$\begin{array}{l} K_2Cy_3\text{—}Co<Cy_3K \\ \qquad\qquad\ | \\ K\ Cy_3>Co\text{—}Cy_3K_2 \end{array}$$

or $K_6, Co^{IV}_2, 4Cy_3$.

This difference of reactions affords the most accurate method of separating nickel from cobalt.

507. It remains only to notice a very curious phenomenon. When to a solution of calcium hypochlorite a few drops of cobaltous nitrate are added, the black sesquioxide immediately precipitates. If, now, the solution is gently heated, oxygen is given off until all the hypochlorite is changed to the calcium chloride.

A very small quantity of the Co_2O_3 is capable of decomposing an unlimited quantity of the hypochlorite, CaO, Cl_2O to $CaCl_2 + O_2$. The alleged reaction is that the hypochlorite changes the Co_2O_3 to CoO_3, a body which is unstable at boiling heat, two molecules decomposing to O_3 and Co_2O_3, and thus becoming capable of removing more oxygen from the hypochlorite.

TESTS FOR NICKEL AND COBALT.—(1) Their dry compounds, mixed with sodium carbonate and heated in the reducing flame before the blowpipe, yield a magnetic powder.

(2) If this powder yields a blue borax bead in the oxidizing flame, which is also persistent in the reducing flame, cobalt is present.

(3) Cobalt is precipitated by potassium nitrite, while nickel is not.

(4) They are best separated by their reactions with cyanogen; but this process is too dangerous to be used except by trained chemists. The cobalt forms a cobalti-cyanide; the nickel forms no corresponding salt.

IRON AND MANGANESE.

508. These metals are also closely related in most of their physical and chemical properties, and are frequently associated together in nature. They act as positive elements in two series of salts: (1) a stable dyad "*ous*" series, correspondent in formula and frequently isomorphous with those of the magnesium group, as $FeCl_2$, $MnSO_4$; (2) a stable tetrad "*ic*" series, containing a double atom in which they are quadrivalent, although apparently trivalent, as $Cl_3{\equiv}Fe{-}Fe{\equiv}Cl_3$ or Fe_2Cl_6. The sulphates form, with alkaline sulphates, alums which are isomorphous with those of the next group, as $K_2O, SO_3 + Fe_2O_33SO_3 + 24H_2O$.

They act also as negative elements, forming salts like K_2MnO_4, which are isomorphous with chromates, as K_2CrO_4. They form, therefore, a connecting link between the pairs of this group.

509. Iron is found native in meteorites, which are sometimes so pure that they can be wrought. In small quantities, its compounds are found every-where; and it is also abundantly found in numerous and thickly distributed mines, which have sometimes almost the dignity of mountains, as in Michigan, Wisconsin, and Missouri.

It is so abundant that its sulphides, arsenides, and other ores difficult of reduction have no commercial value as sources of iron. The reducible ores are its various oxides and carbonates; and these are worked only when found in considerable quantities.

510. The principal of these useful ores are: magnetite, Fe_3O_4 (Fe, 72 per cent); hematite, with its varieties, clay iron stone, specular iron, etc., Fe_2O_3 (Fe, 70 per cent); spathic iron, $FeCo_3$ (Fe, 48 per cent); and black band, a carbonate associated with carbonaceous matters. The working value of an ore frequently depends on the mineral deposits with which it is associated, as coal and lime. One of the best ores of Ohio is a carbonate containing about 40 per cent of iron.

511. These oxy-compounds, if pure, are easily reduced to the metallic state (wrought iron) by smelting with coal. A few so-called "bloomery forges" are now in operation in the United States, producing wrought iron directly from the ore. Generally speaking, the mineral matters with which the ore is mixed require to be separated, and the smelting process becomes more complicated.

The Ordinary Manufacture of Iron.

512. The first stage consists in making *cast iron.* This is effected in tall blast-furnaces, whose shape will be understood from the figure. It is, however, necessary to add that the pipes, t, at the base are called *tuyeres,* through which a blast of cold or of hot air may be driven into the stack.

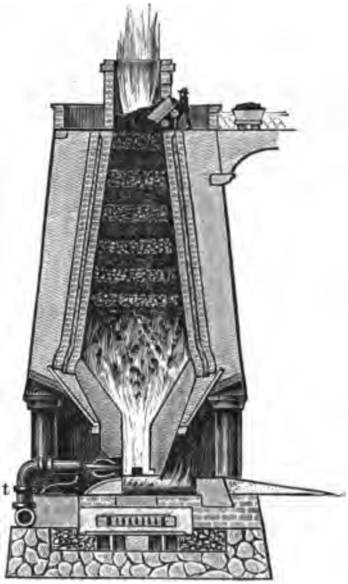


FIG. 92.

We need to consider (1) the nature of the ore. If the ores contain carbonates, they are first roasted to convert them to oxides. This process also serves to expel a portion of the sulphur with which they are frequently contaminated.

(2) The nature of the mineral matters, or *gangue,* with which the ores are associated. It is indispensable that they should be converted into a sort of glass or fusible slag. Hence, if the ores contain clay, they are mixed with lime; or, if they contain an excess of lime, they must be mixed with clay. The most easily fusible slag has nearly the formula, $6CaO, Al_2O_3, 9SiO_2$; and it is desirable to obtain this compound as nearly as possible.

(3) Charcoal yields the best iron; anthracite coal, almost as good. The coal should be free from sulphur, and should not cake in the furnace. Caking coals require to be changed to coke before using. Such cokes lose a portion of their sulphur, and become almost, if not quite, as serviceable as the other forms of carbon.

We have now the crude materials, (*a*) the roasted ores, which are oxides of iron; (*b*) the lime or clay, to render the slags fusible (they are called fluxes); (*c*) some form of carbon, which is to act both as a fuel and as a reducing agent; and (*d*) a blast of air to furnish oxygen to the coal.

In one side the fuel is placed, and the flame is conducted so as to play on the hearth of the other side. Upon this hearth a mixture of iron oxide and white iron is placed. It soon melts and becomes oxidized upon the surface. The mass is now thoroughly stirred (puddled), whereby the carbon is oxidized and escapes as carbonic oxide. As wrought iron is less fusible than cast iron, the mass becomes more and more pasty, until, when the greater part of the carbon has been driven off, it assumes a pasty condition, or "comes to nature," and collects in a spongy mass upon the end of the puddle. It is then taken from the furnace and beaten or squeezed to free it from silicious slags, and becomes welded into an ingot, or bloom, of wrought iron. These ingots are reheated and rolled into bars, to give the metal a homogeneous and fibrous structure.

It is to this fibrous structure that the tenacity of wrought iron is due. Cast iron, when broken, shows a granular structure, and breaks much more easily than wrought iron. It is said that wrought iron loses its fibrous structure and becomes granular by repeated concussions.

518. Wrought iron is never quite pure. The best contains a minute proportion of carbon (from 0.1 to 0.3 per cent); but this can hardly be considered as a disadvantage, because it notably increases the hardness and tenacity of the iron.

Some varieties of bar iron are brittle when cold. This defect is probably due to the presence of phosphorus, and, perhaps, also of silicon. This is called "cold-shortness."

The presence of sulphur, on the other hand, renders the iron brittle when hot. This defect is called "red-shortness." Iron containing both sulphur and phosphorus has both defects, and is difficult to weld when hot, and is brittle when cold.

519. Steel is a product intermediate between cast and wrought iron. It can be cast like pig iron, and worked on the anvil and welded like wrought iron. Moreover, it possesses the invaluable property of receiving a "temper." Soft steel, if suddenly cooled from a high temperature, becomes excessively hard and brittle. By subsequent heating it may be rendered as soft and tenacious as is required. This process is called "drawing the temper."

520. **Steel contains** from 0.5 to 1.5 per cent of carbon. This carbon may be added to wrought iron by heating it for several days at about 1100° C., or below the fusing point of steel, in chests packed with charcoal powder. The product is known as blistered steel, but it is far from being uniform in its composition. When blistered steel is melted and cast into ingots, it becomes homogeneous in structure and is called *cast steel.*

521. **The Bessemer process** converts cast iron into steel by burning away a portion of its carbon.

This is effected by running several tons of melted cast iron into a large crucible, or converter, provided with tuyeres through which a strong blast of air can be blown. Considerable heat is developed by this operation; nearly all of the carbon is burned away, and the iron becomes nearly bar iron. The moment when this result is accomplished may be determined by the spectroscope, or with sufficient accuracy by the practiced eye of the foreman. Then the blast of air is stopped, and a quantity of melted spiegel-eisen, sufficient to furnish the necessary carbon, is added, and the mixture is allowed to rest for a few minutes, to permit all gases to escape, and then it is cast into ingot moulds.

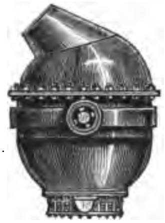


FIG. 94.

This steel is of inferior quality to cast steel, but is admirably adapted for the rails used in railroads, and for other purposes. The presence of $\frac{1}{5000}$ of its weight of phosphorus renders steel brittle.

522. **The malleable iron,** so-called, which is daily growing into use, is simply cast iron which has been

heated for days in boxes packed with the sesquioxide of iron. The cast iron thereby loses enough of its carbon to become assimilated to wrought iron. When the process is well conducted, small objects of brittle white cast iron, as buckles, gate hinges, or even larger articles, become nearly as malleable and tenacious as wrought iron; and small bars so treated may even be drawn into the finest wire. We observe that this is the reverse of the process of making blistered steel. (1) In steel, the carbon is added by heating wrought iron with charcoal; (2) in malleable iron, the carbon is withdrawn by heating cast iron with ferric oxide.

523. Pure iron is readily prepared by heating its oxide in a current of hydrogen or of carbonous oxide. (§ **295**).

In this connection, **Exp. 30** is very interesting.

Exp. 195.—The apparatus necessary will be readily understood from the figure. (Use apparatus in Fig. 27). The hydrogen is carefully dried by sulphuric acid, and allowed to escape until no air remains in the apparatus. The bulb tube, which contains a small quantity of the pulverized oxide, is then heated to redness and becomes reduced: $Fe_2O_3 + 6H = 2Fe + 3H_2O$; or, if carbonous oxide be employed, $Fe_2O_3 + 3CO = 2Fe + 3CO_2$. The reduced iron must be allowed to cool in a current of the gas before the iron is poured out.

524. Iron so reduced is a black powder. It so readily oxidizes that it may be set on fire by a lighted splinter; or, if poured from the reduction tube while warm, takes fire in the air and again changes to the oxide. Pure iron in its compact form is a silvery-white, strongly magnetic metal, exceedingly ductile, malleable, and tenacious, but soft enough to permit its being easily cut with steel files. It fuses at white heat; but, fortunately for the arts, before reaching this temperature it becomes so soft that it may be wrought on the anvil and welded. The blacksmith usually sprinkles sand or borax on the heated metal, in order to form with the oxide film a fusible slag, which may be forced out by the hammer, and thus leave the surfaces clean. They then cohere or weld without difficulty.

525. Iron does not oxidize in dry air at ordinary temperatures. (1) When heated in air, a blackish "scale oxide" forms, which is beaten off by hammering. (2) In moist air, it rapidly oxidizes, or "rusts." The water decomposes, and ferrous oxide forms: this in the presence of carbonic anhydride becomes ferrous carbonate; and this, in turn, becomes ferric hydrate ($Fe_2O_3, 3H_2O$). Unfortunately, this is very porous; and these changes, when once commenced, go on with increasing rapidity until the entire mass is corroded. (3) Heated in a current of steam, iron decomposes water readily; thus, $3Fe + 4H_2O = Fe_3O_4 + 8H$.

Dilute hydrochloric and sulphuric acid dissolve iron readily with evolution of hydrogen, and form respectively ferrous chloride and ferrous sulphate. Dilute nitric acid also dissolves it, evolving nitric oxide and forming, when the action is rapid, ferric nitrate. In strong nitric acid (sp. gr. 1.45) the iron assumes a "passive condition," in which it is neither attacked by the strong acid nor afterward by nitric acid of ordinary strength (sp. gr. 1.35).

526. The uses of iron are so varied and well known that it is useless to attempt to enumerate them. The alloys are not of much importance. When protected from the action of the air by a coating of tin, it forms the tin plate of commerce; and when coated with zinc, it is called galvanized iron.

527. The compounds of iron. Although the two series of iron salts differ widely, they are easily converted from one form to the other. Solutions of ferrous salts quickly oxidize in the air, and soon manifest the presence of ferric salts. They are more quickly oxidized by nitric acid or by a mixture of potassium chlorate and either hydrochloric or nitric acid. On the other hand, reducing agents like nascent hydrogen, sulphuretted hydrogen, stannous chloride, and sulphurous anhydride, convert ferric salts to ferrous.

528. Ferrous salts, when crystallized, have generally a green color and astringent taste. Such as are soluble can be easily made by dissolving iron in the cold dilute acid required.

Ferrous sulphate, $FeSO_4 + 7H_2O$ (*copperas* or *green vitriol*), may be obtained pure from the mixture of iron sulphide and sulphuric acid used in making sulphuretted hydrogen: $FeS + H_2SO_4 = H_2S + FeSO_4$. The remaining solution requires merely to be filtered and crystallized out, preferably under a layer of alcohol. Exposed to the air, the crystals absorb oxygen and form a basic ferric sulphate. Hence, ferrous sulphate may act as a reducing agent, as already noted in gold. It is largely used as a disinfectant.

Ordinary black ink is made from a solution of nut-galls and a sulphate of iron. If ferric sulphate is used, the ink is black when first applied; if ferrous sulphate is used, the ink is first a pale green, but becomes black on exposure to the air.

Ferric sulphate, $Fe_2(SO_4)_3$, is a yellowish, difficultly soluble body, obtained by oxidizing the ferrous sulphate. The basic sulphate is used in making Nordhausen acid.

529. On heating iron wire in a stream of dry chlorine gas, a volatile anhydrous chloride is formed, which collects in the cooler parts of the tube. (1) When the iron is heated to redness, white or yellowish shining scales of ferrous chloride form; (2) at a lower heat, and especially in the presence of air, iridescent spangles of ferric chloride form.

Hydrated ferrous chloride is formed when iron wire is dissolved in hydrochloric acid, and the mixture left to cool in closed vessels. This is changed to ferric chloride by the addition of nitric acid until the solution becomes a yellowish brown. It forms, when dried, a yellow, deliquescent mass. It is also to be noted that both chlorides volatilize even from their solutions when heated.

530. Ferrous carbonate, $FeCO_3$, is probably formed when sodium carbonate is added to a solution of ferrous sulphate; but it soon loses its carbonic anhydride, oxidizes, and yields ferric oxide. It is soluble in an excess of carbonic anhydride, and is found dissolved in mineral waters. It also exists in most blue clays. When these mineral waters are exposed to the air, the ferric hydrate precipitates, sometimes forming an iridescent, oily looking film on the water; and, when such clays are burned, they impart a red color to the bricks, tiles, etc.

531. Iron exhibits strong affinities for sulphur. Ferric sulphide, FeS_2, occurs abundantly in nature as iron pyrites, in yellow, hard crystals strongly resembling gold (fool's gold), but easily distinguished from it by its lower density and superior hardness, and by its giving off sulphurous anhydride when strongly heated in air. This last reaction renders it an available means for the preparation of sulphuric acid.

When a mixture of iron filings and sulphur ($\frac{56}{88}$ Fe, $\frac{32}{88}$ S) are heated together, they combine and form a grayish-black mass of ferrous sulphide, FeS, which is invaluable for the preparation of sulphuretted hydrogen. There are many other sulphides, corresponding to the various oxides.

532. The consideration of the oxides of iron has been reserved to this point, because in them we have valuable tests of iron.

(1) A solution of a ferrous salt, when mixed with a solution of sodium hydrate, yields a white precipitate

of ferrous hydrate, $Fe(OH)_2$, which readily oxidizes in the air—becoming green, then black, and finally reddish brown.

(2) The reddish brown result is ferric hydrate, $Fe_2(OH)_6$. It is obtained directly as a voluminous precipitate by adding sodium hydrate to a solution of a ferric salt. After ignition, it shrinks in volume and is changed to Fe_2O_3. Ammonia produces the same precipitate in ferric salts; but forms with ferrous compounds soluble double salts.

(3) When iron is burned in air, a black compound forms which is principally Fe_3O_4, "scale oxide." This form occurs also in nature, and some specimens of it are natural magnets.

(4) When iron and saltpeter are fused together, and then treated with water, a purple solution is obtained, which is supposed to contain K_2O, FeO_3, potassium ferrate. Ferric anhydride, FeO_3, has never been isolated.

Special Tests for Iron.

(1) When sulphuretted hydrogen is passed through acid solutions of ferric salts, they are reduced, with separation of sulphur, but no further change is produced.

(2) Alkaline sulphides precipitate both ferric and ferrous salts as ferrous sulphide, FeS, a black pulverulent precipitate.

(3) Ammonium sulphocyanide, $(NH_4)CyS$, changes solutions of ferric salts to a beautiful blood-red color, even when the iron is present in very small quantities.

(4) Distinctive reactions are produced when solutions of ferro- and ferri-cyanide of potassium are added to solutions of iron, very slightly acidulated.

	WITH FERROUS SALTS.	WITH FERRIC SALTS.
Ferrocyanide, $K_4(FeCy_6)$	Everitt's White, $K_2Fe''(FeCy_6)$	Prussian Blue, $(Fe^{IV}_2)_2(FeCy_6)_3$.
Ferricyanide, $K_3(FeCy_6)$	Turnbull's Blue, $Fe''_3(FeCy_6)_2$	No precipitate; solution becomes brown.

MANGANESE.

533. Manganese is related not only to zinc, to iron, and to chromium, but probably also to chlorine. It generally occurs in nature as an oxide, MnO_2, Mn_2O_3, or as "*wad*," which is a mixture of these with earthy matters.

The metal is seldom prepared, but may be obtained from its oxide by reducing with carbon at white heat. It is very hard and brittle, slightly magnetic, easily oxidized in moist air, and capable of decomposing hot water.

534. It forms four series of compounds. (1) As a dyad element, salts like $MnCl_2$ or $MnSO_4$, obtained by heating its oxides with hydrochloric or sulphuric acid; as, $MnO_2 + 4HCl = 2H_2O + MnCl_2 + \overset{\frown}{Cl}_2$ or $MnO_2 + H_2SO_4 = MnSO_4 + H_2O + \overset{\frown}{O}$. These salts are pinkish colored, and crystallize in forms isomorphous with zinc salts, as $MnSO_4 + 7H_2O$. They are the usual compounds in which manganese acts as a positive element. Their solutions, when treated with sodium hydrate, yield a white precipitate of hydrated manganous oxide, which rapidly oxidizes in the air, and finally becomes brown $Mn_2O_3, 3H_2O$. When ammonium sulphide is added to solutions of these salts, it forms flesh-red manganous sulphide, MnS, a characteristic test, not only by reason of its color, but also because it is the only sulphide of the group which is soluble in acetic acid.

(2) As a tetrad element, in oxides like MnO_2 (*pyrolusite*); or with a double atom like Mn_2O_3 (*Braunite*). These, when heated with hydrochloric acid, yield free chlorine and form manganous chloride.

There is, besides, an unstable green sulphate of this group, which forms a moderately stable alum with alkaline sulphates, as $K_2O, SO_3 + Mn_2O_3, 3SO_3 + 24H_2O$.

(3) As a hexad element, neither MnO_3 nor $MnCl_6$ are known; but, when any oxide of manganese is fused with saltpeter, a deep-green, easily soluble mass is obtained, which is potassium manganate, K_2O, MnO_3 or K_2MnO_4. This body is so unstable that it is easily decomposed by water or by acetic acid, forming a rose-red solution of the permanganate.

(4) The potassium permanganate has the formula K_2O, Mn_2O_7 or $KMnO_4$. As this salt is isomorphous with the potassium perchlorate $KClO_4$, it is supposed that manganese acts in this as a septad element like chlorine.

535. Potassium permanganate crystallizes in beautiful red rhombic prisms, freely soluble in water. It is more stable than the manganate, but both are strong oxidizing agents, readily giving up most of their oxygen and reverting to manganous oxides, especially in the presence of free acids. Hence, the potassium permanganate is much used in volumetric analysis.

Exp. 196.—Acidulate a solution of a ferrous salt, and add drop by drop, a solution of a permanganate. The red color of the permanganate solution does not remain permanent until all the ferrous salt has been oxidized to ferric:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Hence, if the quantity of the permanganate used is known, that of the ferrous oxide present can be calculated.

From the readiness with which both the manganate and permanganate salts are decomposed, they are used as disinfecting agents. They are especially useful in detecting the presence of decomposing organic bodies in waters used for drinking.

536. The uses of manganese are chiefly (1) in the preparation of the disinfecting agents already mentioned; (2) in making glass, to which it imparts an amethyst color when alone, or, when mixed in the required amount, destroys the green color produced by iron; (3) in the preparation of chlorine used in the manufacture of bleaching powder.

TESTS.—Some of the tests for manganese have already been indicated. The most characteristic are the flesh-red sulphide and the potassium manganate formed by fusion with niter.

In its other reactions it agrees generally with the members of this group, except that its white hydrate in alkaline solutions is more readily oxidized by air or by chlorine to the brown sesquioxide, Mn_2O_3.

CHROMIUM AND ALUMINIUM.

537. **These elements** are closely related to iron. Chromium is considered first, because it forms a series of dyad compounds represented by $CrCl_2$ and the double sulphate, $K_2O, CrO, (SO_3)_2 + 6H_2O$. These chromous compounds are generally unstable; and chromous chloride is so readily changed to its higher compounds that it is one of the most powerful reducing agents known. They are also seldom met with, and will not be considered further. It also forms an unimportant oxide, Cr_3O_4, resembling magnetite.

538. **In the tetrad series,** both of these elements, Al_2O_3 and Cr_2O_3, form salts which strongly resemble ferric salts, and are isomorphous with them. The only oxide of aluminium is Al_2O_3, which acts both as a weak base and as a weak acid.

Chromium forms also a hexad series, like iron and manganese. In this series it acts as a negative element, as K_2O, CrO_3

539. **The most important ore of chromium** is chrome iron, $FeCr_2O_4$, or, perhaps, FeO, Cr_2O_3. It also occurs in a few other minerals as red lead ore, $PbCrO_4$, and is the green coloring principle of the emerald.

Metallic chromium has no use in the arts, and is seldom prepared. It is one of the most infusible of metals, and so hard as to scratch glass. Combined with steel, it forms an exceedingly hard alloy, which has found employment in cutting glass, sharpening knives, and in making drills.

540. The compounds of chromium. Unlike the metals previously studied, chromium ores are worked only for the sake of their salts. The first formed are the chromates; the other salts are derived from them by subsequent treatment.

The pulverized chrome iron ore is mixed with potassium carbonate and potassium nitrate, and is then heated in a current of air on the hearth of a reverberatory furnace. The Cr_2O_3 is oxidized to $2CrO_3$, and unites with the potassium to form potassium chromate.

541. Potassium chromate, K_2O, CrO_3. This salt is obtained by lixiviating the ignited mixture and evaporating the solution. It forms very soluble, yellow, rhombic crystals.

542. Potassium bichromate, $K_2O, 2CrO_3$ or $K_2Cr_2O_7$, is the usual salt found in commerce. It is prepared by mixing the solution of the chromate with nitric acid: $2(K_2O, CrO_3) + H_2O, N_2O_5 = H_2O + K_2O, N_2O_5 + K_2O, 2CrO_3$. The salt is soluble in 10 parts of water, and crystallizes in beautiful red, tabular prisms. With an excess of nitric acid, a red ter-chromate is also formed, $K_2O, 3CrO_3$.

543. Chromic anhydride, CrO_3, is obtained by mixing a saturated solution of the bi-chromate with a little more than its own bulk of sulphuric acid. When this mixture cools, the chromic anhydride separates out in crimson needles. These crystals are deliquescent, and are very soluble in water. Although a moderately stable body, it is a powerful oxidizing agent, and is instantly reduced by organic matters and by all reducing agents, as H_2S, SO_2, Zn, and even by HCl. Hence, its solution can not be filtered through paper, and the crystals formed as above described must be separated from the mother liquor by decantation, and dried upon a porous tile.

Exp. 197.—Place upon a saucer dry chromic anhydride, and pour upon this a little alcohol. The CrO_3 is reduced partly to Cr_2O_3 and partly to CrO_2; the alcohol is changed to *aldehyde:* $3(C_2H_6O)$ alcohol $+ 2CrO_3 = 3H_2O + Cr_2O_3 + 3(C_2H_4O)$ aldehyde. So much heat is evolved that the alcohol is frequently set on fire.

544. Chromic acid, H_2O, CrO_3 or H_2CrO_4, has never been isolated; but there is a large number of chromates which are generally yellow or red salts. Many of these are used as pigments, and are easily obtained by mixing a solution of potassium bi-chromate with a solution of a salt of some other metal.

(1) With lead acetate, $PbCrO_4$ forms as a beautiful yellow precipitate, which is "chrome yellow." "Chrome green" is a mixture of this with Prussian blue.

(2) With barium chloride it forms a pale yellow precipitate of $BaCrO_4$, which is "yellow ultramarine."

(3) With silver nitrate and with mercurous nitrate, the products are red chromates, which are beautiful colors, but too expensive to be used as pigments.

There are numerous other chromates, most of which, except those of the alkalies and of strontium, calcium, and magnesium, are insoluble in water. They are all decomposed by heat, with evolution of oxygen.

545. Lead chromate is used as an oxidizing agent in organic analysis. When heated with sulphuric acid, the chromates are reduced with evolution of oxygen—*e. g.*, $2CrO_3 + 3H_2SO_4 = Cr_2O_33SO_3 + 3H_2O + 3\overset{\frown}{O}$; and by hydrochloric acid, with evolution of chlorine:

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 6\overset{\frown}{Cl}.$$

These last reactions will take place when a chromate is heated with these acids, and an excess of acid must be used in order to combine with the base of the chromate.

546. There are also several compounds of this series, of great theoretical interest. One of these is CrO_2Cl_2, in which two chlorine atoms have displaced one atom of oxygen. It is obtained by distilling a mixture of common salt and sulphuric acid with potassium bichromate, as a blood-red liquid, which is a powerful oxidizing agent, commonly called *chlorochromic anhydride.* At the same time, there forms a salt which is $K_2Cr_2O_6Cl_2$, or a potassium bi-chromate in which one atom of oxygen is replaced by two atoms of chlorine.

547. Chromium acts as a negative element in this series. It also acts as a positive element in a totally different series. *Chromic oxide,* Cr_2O_3, is obtainable as an amorphous green powder by igniting chromic anhydride, or by igniting any chromate containing a volatile base, as NH_4 or Hg. It is used as a green pigment, and is especially valuable for imparting a beautiful green color to glass and porcelain. This oxide is almost insoluble in acids.

548. The other compounds of this series are most easily prepared from chrome alum. Chrome alum is itself made (1) by heating a mixture of potassium bichromate and sulphuric acid with alcohol; or (2), better, by passing through the mixture, in the cold, a stream of sulphurous anhydride: thus, $K_2O,2CrO_3+H_2SO_4+3SO_2=H_2O+(K_2O,SO_3+Cr_2O_3,3SO_3)$. On crystallizing, splendid dark purple octahedra form, which contain $24H_2O$, or are $KCr(SO_4)_2+12H_2O$.

549. Chromic hydrate, $Cr_2O_3,3H_2O$, may be precipitated from a solution of chrome alum by any alkaline hydrate. It is a bulky, greenish-blue powder, soluble in excess of soda or potash, but is again precipitated on boiling. It is a feeble base, but is remarkable for forming with the acids two classes of salts, which are identical in formulæ, but differ in some of their properties. (1) Violet salts formed (when a rise in temperature is avoided) by dissolving the hydrate in acids. These salts are crystallizable, and are insoluble in alcohol. (2) Green salts, which are obtained on boiling the violet salts. They are uncrystallizable, but are soluble in alcohol. The green salts, when kept in solution for months, gradually recover their violet color and become crystallizable. These are marked examples of isomerism among inorganic compounds.

550. Chromic sulphate, $Cr_2(SO_4)^3 + 18H_2O$, is obtained by dissolving chromic hydrate in dilute sulphuric acid. If prepared in the cold, it has a violet color; but, when heated, becomes green, reverting after a time in solution to the violet modification.

551. Chromic chloride, $Cr_2Cl_6 + 12H_2O$, forms when chromic hydrate, or any chromate, is dissolved in hydrochloric acid. An anhydrous chloride of a beautiful peach-blossom color, which is scarcely soluble in boiling water or in acids, is formed when chlorine gas is passed over ignited chromic oxide.

It is also supposed that there is a perchromic acid, H_2O, Cr_2O_7, which is formed when peroxide of hydrogen is added to chromic salts. A blue solution is thereby formed, which is a delicate test for chromium; but neither the acid nor its salts have been obtained.

552. Uses of chromium. The chromates are valuable oxidizing agents, especially in the presence of sulphuric acid. Potassium bichromate solution is frequently used in galvanic batteries. Principally, however, chromium compounds are used in dyes and pigments. They are generally yellow or green. The green printing ink used in "green-backs" owes its color to chromium.

Tests for Chromium.—(1) All chromium compounds, when heated with borax, yield an emerald-colored bead which is very characteristic.

(2) All chromium compounds, when fused with soda and niter, yield a yellow chromate soluble in water.

(3) These chromates, neutralized with acetic acid, yield characteristic precipitates: yellow with lead and barium; red with silver and mercurous salts.

(4) The chromates in solution are reduced to salts of the sesqui-oxide by sulphuretted hydrogen. These reduced solutions, or solutions of salts of the sesqui-oxide, yield, with ammonium sulphide or ammonia, greenish or bluish hydrates, somewhat soluble in excess of the precipitant, but again precipitated upon boiling.

ALUMINIUM.

553. Aluminium is one of the most abundant and most widely distributed of the elements. It never occurs native, and seldom occurs as an oxide (emery, corundum), but more frequently as a fluoride (cryolite). It forms, however, an almost endless variety of double silicates, which constitute the great majority of the rocks of the earth, as granite, basalt, slates, shales, and clays. The feldspars and micas are silicates of alumina combined with silicates of potash, or soda, or lime, or magnesia, or a mixture of these with small amounts of other bases. When such minerals as these disintegrate by the action of atmospheric agencies, ordinary clays, potter's clay, fire clay, and kaolin are formed, which are aluminic silicates, more or less contaminated with other substances. Alumina is also a constituent of several precious stones, as the sapphire, ruby, topaz, emerald, and garnet.

554. Aluminium is best prepared by fusing the double chloride of aluminium and sodium with metallic sodium: $2NaAlCl_4 + 6Na = 8NaCl + 2Al$. The addition of cryolite ($Al_2Na_6F_{12}$) facilitates the reduction. It is a bluish-white metal, of very low specific gravity (2.56), which is quite malleable, ductile, and tenacious. It is also remarkably sonorous, which property it also communicates to many of its alloys. Aluminium is not oxidized in the air nor affected by sulphuretted hydrogen. It is not attacked by cold dilute sulphuric and nitric acids, but dissolves readily in hydrochloric acid and in solutions of caustic soda and potassa.

Its many valuable properties render it desirable that it should be more abundantly used in the arts and in the various appliances of the household; but the cost of its preparation (which is dependent on the price of sodium) has restricted its application mainly to the construction of delicate balances, small weights, and other instruments in which lightness is desired and only a moderate strength needed.

Much has been hoped for the alloys of aluminium. Aluminium bronze contains 9 parts of copper and 1 part of aluminium. It is very strong, difficultly fusible, unaltered in air, but has not found a wide application in the arts.

555. The compounds of aluminium. As already stated, aluminium forms but one series of compounds, the tetrad, represented by Al_2O_3 and by Al_2Cl_6.

Alum is the most important salt. The simplest process by which it is manufactured consists (1) in forming aluminium sulphate by heating a pure clay or shale with sulphuric acid. On lixiviating this mass, an aluminium sulphate is obtained: $Al_2O_3, 3SO_3 + 18H_2O$. (2) Because this salt is difficultly crystallizable, it is converted into a double salt containing either K_2O, SO_3 or $(NH_4)_2O, SO_3$, which crystallizes in beautiful octahedra, in a condition which insures the purity of the commercial article. This is effected simply by mixing the solution of aluminium sulphate with the requisite amount either of potassium or of ammonium sulphate, and allowing the solution to crystallize. The crystals have the formula $K_2O, Al_2O_3, 4SO_3 + 24H_2O$ and

$(NH_4)_2O, Al_2O_3, 4SO_3 + 24H_2O$; or, written in molecular formulæ,

$$KAl(SO_4)_2 + 12H_2O \text{ and } NH_4Al(SO_4)_2 + 12H_2O.$$

Formerly, potassium alum was the most common; but now the ammonium alum has become the usual commercial article, because the ammonium sulphate is obtained at a low price from the refuse liquors of gas works. The value of either alum depends only on the amount of aluminium sulphate it contains.* Of late years, aluminium sulphate has found its way into commerce under the name of concentrated alum.

556. Aluminium hydrate, $\overset{\cdot}{A}l(OH)_3$, is formed as a white gelatinous precipitate when ammonia or (avoiding excess) any other alkali or alkaline carbonate is added to a solution of alum. With a small amount of alkaline carbonate, a basic sulphate, Al_2O_3, SO_3, is formed. The use of alum in the arts depends upon the fact that both the hydrate and the basic salt have the power of combining with the coloring principles of organic dyes, like cochineal, to form insoluble pigments called lakes, as carmine.

In applying this reaction to calico printing, (1) the stuffs are dipped in a solution containing this basic alum, when the cloth becomes impregnated with the aluminium compound. (2) By the action of air or of steam, the aluminium becomes firmly incorporated with the fibers of the cloth. This is the "ageing process." (3) The cloth is now dipped into the dye-vat, and the aluminium combines with the coloring matters and fixes them within the fiber. Such colors are likely to be "fast," that is, durable; and the alumina is said to act as a "mordant," because it bites or holds the colors.

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* The word alum, which was once used specifically to denote potash alum, is now generically applied to all double sulphates which crystallize in octahedra with $24H_2O$, and contain a monad sulphate together with a tetrad sulphate; thus, $R'_2O, SO_3 + R^{IV}_2O_3, 3SO_3 + 24H_2O$. In this way we may have a large series of iron, chromium, and aluminium alums with either of the alkalies, potassium, sodium, etc. There are also a number of pseudo-alums with $22H_2O$, containing dyad metals like magnesium.

Aluminium hydrate is easily soluble in dilute acids, forming salts such as $Al(NO_3)_3$; Al_2Cl_6. The chloride forms a number of double salts with the alkaline chlorides.

557. Aluminium oxide, Al_2O_3, or *alumina*, occurs in nature nearly pure in corundum, and in an impure state as emery. Both of these are extremely hard, and are used for polishing. It is artificially obtained as a white amorphous powder by igniting aluminium hydrate or ammonia alum. It is then an almost infusible mass, and is insoluble in acids. It is rendered soluble by fusion with carbonates of soda or of potash. The compounds thus formed are aluminiates, in which the aluminium acts as a negative element.

558. Potassium aluminiate, K_2O, Al_2O_3 or $KAlO_2$, is crystallizable; *sodium aluminate* is a white amorphous solid. Solutions of either of these are decomposed by acids, even by carbonic, forming aluminium hydrate. Hence, they may be used as substitutes for alum.

The affinities of aluminium in both these classes of salts are very feeble; for, if a solution of an aluminium salt is mixed in atomic proportions with one of an aluminiate, both are decomposed with the formation of aluminium hydrate; for example:

$$Al_2Cl_6 + 6KAlO_2 + 12H_2O = 4Al_2O_3, 3H_2O + 6KCl.$$

559. Ultramarine, a beautiful blue pigment, was formerly obtained from *lapis lazuli*, one of the precious minerals. After careful analyses of the mineral, attempts were made to reproduce the pigment artifically, by fusing together the materials in the proportions so ascertained. Finally, it was found that by fusing together pure clay, sodium sulphate, and charcoal, a green "ultramarine" was produced which is a valuable pigment. This product, mixed with sulphur and again fused, yields a blue ultramarine which fairly rivals in brilliancy of color the native mineral, and is much cheaper.

This may be considered as one of the triumphs of chemistry; although, even now, the cause of the beautiful blue color in either the native or artificial ultramarine has not been satisfactorily ascertained. We know only that they contain sodium-aluminium silicates and sodium polysulphide as their principal ingredients.

560. Aluminium silicates are of great importance. They are seldom found pure in nature, being generally contaminated with iron and other bases. The purest is kaolin, a white friable clay derived from the decomposition of feldspars. These clays are used in the manufacture of porcelain; the more impure clays, in the manufacture of bricks.

Limestones containing about 20 per cent of aluminium silicate when calcined yield hydraulic cements, which have the property of hardening under water.

TESTS.—(1) Solutions of aluminium salts are precipitated as white gelatinous hydrates, $Al(OH)_3$, by ammonium hydrate and ammonium sulphide, almost completely.

(2) The hydrate, when moistened with cobalt nitrate, and ignited, forms an infusible blue mass.

Gallium, discovered by Lecoq de Boisbaudran in 1875, is probably related to aluminium. It has been obtained in whitish octahedral crystals (sp. gr. 5.9), which, though harder than iron, melt at a temperature of about 30°C. Its atomic weight has not been determined (68?).

Recapitulation.

The elements in this group form compounds in which they enter as dyads, tetrads, and hexads.

The dyad compounds strongly resemble those of Mg, Zn, and Cd, being isomorphous with them, and capable of replacing them in the double salts with the alkalies, as in $R'_2O, SO_3 + R''O, SO_3 + 6H_2O$. All these dyad compounds are precipitated by sodium hydrate, avoiding excess, as white or greenish hydrates, soluble in a large excess of ammonium chloride. H_2S does not precipitate Mg; it precipitates CdS in acid and alkaline solutions, and the others only in alkaline solutions or by alkaline sulphides, as sulphides. Their protoxides are generally strong bases.

The hydrates of the tetrad series are weak bases of the formula $R^{IV}{}_2O_3, 3H_2O$. They are precipitated on adding to their neutral solutions almost any dyad carbonate. The best reagent is $BaCO_3$. They do not dissolve in ammonium chloride, and hence are also precipitated by NH_4HO. These hydrates also in some cases act as weak acids. Their sulphates form with alkaline sulphates double salts containing $24H_2O$ (alums). Cr and Al do not form sulphides in the wet way.

Some of these elements form also a hexad series, in which they act as negative elements. The best representatives of this class of compounds are the salts of the acids of manganese and chromium, as K_2MnO_4, K_2CrO_4.

These three series differ widely from each other. Al forms only tetrad compounds. The dyad compounds of the others are changed by oxidizing agents to tetrad compounds; some (not all) of the tetrads may be further oxidized by fusion with niter to hexad compounds. On the other hand, reducing agents will convert hexads to tetrads, and most tetrads to dyads. These elements therefore exhibit a very flexible character.

It is not improbable that Mn and Cr also act as heptads in $KMnO_4$ and in perchromic acid.

The metals of this group have important uses in the arts; iron being, perhaps, the most used and the most useful metal known. Many of their alloys and salts find important applications in the arts. Fe, Co, Ni, and Mn are magnetic elements.

It may also be noted that while these elements agree in some particulars, they differ in many others. Some form by preference dyad compounds; Al only tetrad; Cr is best known as a hexad. Nevertheless, the pairs which make up the sub-groups are strongly related.

CHAPTER XVI.

KERAMICS AND GLASS.

561. Bricks are made from clay. This is kneaded with a small amount of water, so as to render the mass homogeneous; then moulded into shape; then thoroughly dried in the open air; and, finally, burned.

Not all varieties of clay are suitable for this purpose. All clays shrink on drying; but the very plastic clays, which are composed for the greater part of aluminium silicate, shrink so much that they crack and fall into pieces. Hence, an admixture of sand is necessary, which must be supplied, if not naturally present in the clay, in order to give the right consistence to the mass. In tropical countries, the bricks are not burned, but are only sun-dried. These are at best very friable, and are suitable only for low structures.

A small quantity of lime or of feldspar is also a useful constituent of the clay; for, when the bricks are burned, these substances fuse and serve to cement the particles of the clay together. An excess of lime renders the bricks too brittle.

When the clays contain no ferrous carbonate, the bricks, when burned, have a yellow color. The red color of ordinary bricks is due to the conversion of the ferrous carbonate to the ferric oxide, by the action of the heat and the atmospheric oxygen.

Fire-bricks are made from clays which contain neither lime nor iron. These clays fuse less easily than the impure varieties, but they are also capable of resisting the action of fire, and are therefore employed for the lining of furnaces and for crucibles.

All bricks are porous, excepting the few that are burned in immediate contact with the fire. These become so over-heated that their materials fuse and form a sort of glaze over their surface.

The so-called terra-cotta wares are made in the same manner, except that a greater care is taken in moulding the clay and in burning.

562. Ordinary pottery is made from the better qualities of clay mixed with sand. Drain pipes and tiles are fashioned by machinery. Most of the hollow vessels are fashioned by hand upon a potter's wheel. The articles are then allowed to dry very slowly. When thoroughly dry, they are baked in kilns. Porous goods, like drain pipes and flower pots, receive no further treatment. Stoneware vessels are glazed in a very simple manner by a process known as salt glazing.

The ware is coated with a thin film of sand by dipping into a mixture of fine sand and water. It is then intensely heated in the kiln, and a quantity of damp salt thrown in. The joint action of the steam and the salt converts the sand into sodium silicate, which fuses to a glass on the surface of the ware.

Other of the cheaper forms of pottery are glazed by dipping the wares into a mixture of clay and litharge. This fuses in the kiln to a lead glass.

563. Porcelain. In the manufacture of porcelain, especial care is taken in selecting a nearly pure aluminium silicate: this is kaolin. But it is too infusible a substance to be used alone, and, therefore, requires the addition of some more fusible material, as feldspar. The Vienna porcelain and "china" contain quartz also.

The materials are first ground together, mixed with water, and moulded like ordinary pottery into any required shape, and then are allowed to dry slowly in the air. These dried vessels are then burned in kilns, in which a high temperature may be obtained, and are thereby baked to a white, porous body, which is incorrectly termed biscuit ware. It then requires to be glazed. The best glazing is obtained by dipping the biscuit ware in water containing a mixture which very nearly resembles the original materials, only a little more fusible, and sometimes containing chalk or gypsum. The ware is again reheated to a temperature sufficiently high to fuse the glaze, and is then ready for market.

There are several varieties of porcelain: (1) a very hard sort, like that of China and Japan, which contains a notable amount of quartz; (2) a softer sort, like that of Sevres, which is quite translucent. This translucency is secured by the admixture of "*fritt*" (which consists of a vitrified mixture of sand and alkaline materials) to the kaolin. (3) The English porcelain, which is quite hard but opaque, contains a large proportion of calcined bones.

In the less valuable varieties of porcelain, the glaze frequently contains lead or boracic acid mixed with the silicates. This glazing requires a less temperature for fusing in the second baking; but it is liable to crack, because it is not homogeneous in structure with the body.

564. Glass requires that the materials of which it is composed should be capable of being thoroughly fused together, and, on cooling, yield an amorphous, transparent mass, not easily affected by water or by atmospheric agencies. It is a mixture of various silicates, of which the most common are those of lime, sodium, and potassium.

The cheapest variety of glass (*bottle glass*) is a double silicate of alumina and lime. This mixture is so difficultly fusible that sodium silicate is generally added. The other varieties of glass either contain no alumina or a very small quantity.

Ordinary *window glass* is a mixture which may be very nearly represented by the formula, $Na_2Ca\,4SiO_3$.

The materials used in its preparation are clean white sand, slaked lime, and sodium carbonate; or, instead of the last, a mixture of sodium sulphate with sufficient charcoal to decompose the sulphuric acid. All sodium glasses have a bluish tinge, from which potassium glass is free.

The best *plate glass* is also chiefly a silicate of soda and lime, but also contains potassium silicate.

Crown glass and *Bohemian glass* contain no soda. They have approximately the formula, $K_4Ca_815SiO_8$. They are beautiful, clear glasses, well adapted for optical purposes.*

Flint glass is a double silicate of potassium and lead prepared by fusing together the purest white sand or flint, calcined and ground, with lead oxide and refined pearl ash. Other materials are also added in small quantities, to prevent the reduction of the lead (KNO_3), or to remove the color which would be produced by the presence of iron (As_2O_3 or MnO_2). Its approximate formula is $K_4Pb_810SiO_8$. The presence of the lead silicate greatly increases the fusibility of the glass, and also adds to its luster and beauty. It is much used for ornamental purposes, as fine cut glass.† In optical instruments, lenses of flint and crown glass are frequently combined to form achromatic lenses. The dispersive powers are made to neutralize each other, and yet leave a considerable index of refraction.

Other silicates are frequently used in glass, as baryta and zinc. Sometimes, also, a quantity of boracic acid is used to replace a portion of the silica.

565. Many metallic oxides impart characteristic colors to glass. Ferrous silicate produces a green glass; ferric silicate, a yellow which is hardly noticeable when in small quantities. Hence, except for green bottle glass, it is desirable to oxidize the iron which is scarcely ever absent from the sand. This is effected by niter, arsenious oxide, or red lead. Manganese binoxide also decolorizes green ferrous silicate; but it is a disputed question whether it effects the change by acting as an oxidizing agent, or by producing a glass of a complementary color, since by itself it yields an amethyst purple glass.

The agents used to impart colors to glass are principally these: red, Cu_2O; ruby, purple of Cassius (Au); amethyst, MnO_2; blue, CoO; green, FeO, Cr_2O_3, CuO; yellow, Sb_2O_3; greenish yellow, U_2O_3. An excess of lead oxide also produces a yellow glass.

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* Index of refraction, 1.53; coefficient of dispersion, 0.02.

† Index of refraction, 1.64; coefficient of dispersion, 0.04.

566. The manufacture of glass can only be sketched.

The materials are fused together in large pots made of fire-clay, and are then permitted to remain for some time to allow air-bubbles to escape, and to remove the glass scum which rises to the surface. It is then taken from the pots and wrought into the shape required. Much of our glass-ware is blown, as bottles. Tumblers, glass plates, etc., are generally moulded.

All glass-ware, after being shaped, requires to be carefully annealed. This is effected by a process of slow cooling. The hot ware is passed through a long chamber so arranged that the heat is gradually diminished, and the glass is taken from the extreme end quite cool. Unannealed glass is very liable to crack with sudden changes of temperature.

Cut glass receives additional treatment, being ground and afterward polished on emery wheels.

Recapitulation.

Bricks, ordinary pottery, and porcelain require that the materials used (clay, kaolin) should be difficultly fusible.

These materials are kneaded together, dried, and baked. Stoneware and porcelain are then covered with a glaze, and baked a second time.

Glass requires that the materials used should be easily fusible, and furnish a transparent mass.

Glass requires no second baking, but requires a careful annealing.

CHAPTER XVII.

CRYSTALLOGRAPHY.

567. Solid bodies are either *amorphous* or *crystalline.* Amorphous bodies are those which have no well-defined geometrical form, as chalk, clay, starch. Crystals have regular, geometrical figures, bounded by flat surfaces called planes. Although the number of such figures is very great, it is possible to group them all into six primary forms, in each of which the bounding planes are supposed to be symmetrically disposed about imaginary lines called axes. These axes are generally three, which intersect each other in the center of figure.

I. *The isometric or regular system* has all the three axes at right angles to each other, and all equal in length. Such are the regular octahedra, represented by the alums; and the cubes, represented by common salt.

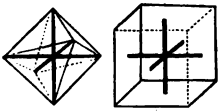

FIG. 95.

II. *The quadratic or tetragonal system* has all the three axes at right angles to each other; but of these, only the two lateral axes are equal in length. No cubes are possible in this system, but they are replaced by vertical square prisms. The octahedra of this system may have either form shown in Fig. 96, or the vertical axis may be shorter than the lateral axes.

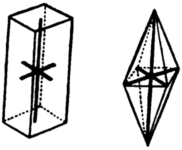

FIG. 96.

III. *The hexagonal system* has four axes. The three lateral axes are in the same plane, equal in length, and inclined to each other at an angle of 60°. The vertical axis is perpendicular to these, and may be either longer or shorter than they. Neither cubes nor octrahedra are possible in this system. We may have six-sided prisms, like quartz; or rhombohedra, like Iceland spar.

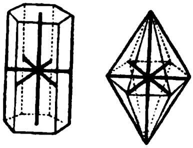

Fig. 97.

IV. *The ortho-rhombic or prismatic system* has three axes all at right angles to each other, but all unequal in length. Fig. 98 represents an octohedron of sulphur crystallized in the cold.

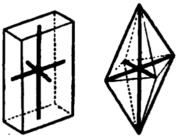

Fig. 98.

V. *The monoclinic system* has three axes which may all differ in length. The two lateral axes are at right angles to each other; the vertical axis is perpendicular to one lateral axis and oblique to the other. Sulphur crystallized after fusion, and sodium sulphate, are examples.

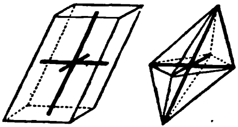

Fig. 99.

VI. *The triclinic or doubly oblique system* has three axes which are all unequal and obliquely inclined to each other. Such, for example, are crystals of cupric sulphate.

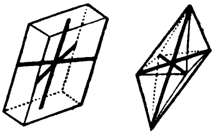

Fig. 100.

Note.—The student will do well to remember that these are the primary forms of crystals. The derived forms are so numerous that it would require a large treatise to describe them.

568. Some bodies crystallize in two forms, as sulphur. These are said to be dimorphous. When different bodies crystallize in the same form, they are said to be isomorphous. Such are the arseniates and phosphates of the same metal.

The word crystalline is often applied to bodies which are apparently made up of small interlaced crystals that can not be separated, but which are semi-transparent, as quartz rock.

PROBLEMS.

COMPARISON AT 29.92 INCHES (760 mm.) BAROMETER.

	32° F. = 0° C.					60° F.	
	WEIGHT OF 1 LITRE IN GRAMMES.	VOLUME OF 1 GRAMME IN LITRES.	SPECIFIC GRAVITY.		WEIGHT OF 1 GALLON IN GRAINS.	WEIGHT OF 100 CUB. IN. IN GRAINS.	VOLUME OF 1 GRAIN IN CUB. INCHES.
			AIR = 1.	H = 1,			
Air . .	1.2932	0.77	1.	14.43	71.604	30.954	3.23
Hydrogen	0.0896	11.19	0.0693	1.	4.947	2.14	46.73
Water .	at 4° C. 1000.	.001	773.2 at 15°C. 819.	11160.	pounds. 8.3456	25245.6 at 4° C. 25287.9	.00396

Note.—These problems are intended only as hints of work that may be done. The teacher may extend them indefinitely; and may add also such problems as involve specific gravity, specific heat, calorific power, etc. The problems are carefully graded; and if the student attacks them in the order given, he will find little difficulty in solving them. It is taken for granted that the bodies used are chemically pure, and that there is no loss in manipulation.

1. What is the weight of one cubic centimetre of each of the following substances, at the normal temperature and pressure?

(*a*) H; N; O; Air; Cl; CO; CO_2.
(*b*) H_2O; CS_2; H_2SO_4; HNO_3; Br.
(*c*) Li, K; Fe; Ag; Au; Pt.

What is the weight of one litre of each of the above? What is the bulk, in cubic centimetres, of one gramme of each of the above?

Note.—The Law of Charles is that *the volumes of all gases are proportional to their absolute temperature.* This temperature is reckoned from —273° C., and is therefore equal to their recorded temperature above zero + 273° C.; *e. g.*, the absolute temperature of air at 27° C. is 300° C.; and, at 127° C. is 400° C. Therefore, if a given weight of air measured one litre at 300° C., it would measure $\frac{400}{300} = 1.33$ L. at 400° C.

2. What is the volume of one cubic centimetre of the gases in Ex. 1, when reckoned at 100° C.? At 50° C.?

Note.—The Law of Mariotte is that *the volume of a gas is inversely proportioned to the pressure to which it is subjected; e. g.*, if a litre of air taken at a pressure of one atmosphere, or 760 mm. barometer, is subjected to the pressure of two atmospheres, it will be condensed to $\frac{760}{760 \times 2} = \frac{1}{2}$ of its former value; or, if the pressure is diminished to 570 mm., the volume will be increased to $\frac{760}{570} = \frac{4}{3}$ of its original volume.

3. What will be the volume of each of the gases in Ex. 1, when taken under a pressure of 1140 mm.? Of 380 mm.?

4. What will be the volume of each of the same gases reckoned at 100° C., and under a pressure of 950 mm. bar.?

5. What is the weight of each element in one gramme of H_2O? What is the bulk of each in this weight taken at 0° C.? What is the bulk of each taken at 100° C.? What will be the volume of the steam formed by their combination, (*a*) reckoned at 0° C.? (*b*) At 100° C.? How much pressure will be required to reduce the latter volume to the volume at 0° C.?

6. Given one gramme each of the following gases, HCl, H_2S, H_3N, CO_2, required—

(*a*) The weight of each of the elements forming these compounds. (*b*) The volume of each element. (*c*) The volume of the compound.

7. From the data given on p. 35, calculate how many cubic centimetres of water will be required to form a saturated solution containing one gramme of these gases. What will be the weight of the gas absorbed? What will then be the weight of the solution? Could the volume of the solution be calculated from the data given? Has the temperature or the pressure any effect upon the amount of the gas absorbed?

8. How many grammes of each element in 100 grammes of each of the following? H_2O; FeO; Fe_3O_4; Fe_2O_3; $FeCO_3$; $FeSO_4$; $FeSO_4, 7H_2O$. Are your answers percentages?

NOTE. — To calculate the empirical formula of a compound, (1) *find its percentage composition;* (2) *divide each constituent by its atomic weight;* (3) *reduce the quotients so obtained to their simplest ratios.*

9. Water yields in 100 parts:

$$\begin{array}{llcl|c} & & & & \text{RATIOS.} \\ H & 11.11 \div 1 & = & 11.11 & 2 \\ O & \underline{88.88} \div 16 & = & 5.55 & 1 \\ & 100. & & & \end{array}$$

The formula is, therefore, H_2O. Calculate the formulæ from the following data:

$$\begin{array}{lll} (a) & N & 82.35 \\ & H & 17.65 \\ \hline & & 100. \end{array} \qquad \begin{array}{lll} (b) & Fe & 70. \\ & O & 30. \\ \hline & & 100. \end{array}$$

$$\begin{array}{lll} (c) & K & 28.73 \\ & H & 0.73 \\ & S & 23.52 \\ & O & 47.02 \\ \hline & & 100. \end{array} \qquad \begin{array}{lll} (d) & Cu & 57.46 \\ & C & 5.43 \\ & H & 0.91 \\ & O & 36.20 \\ \hline & & 100. \end{array}$$

10. How many grammes of Cu are required to make 100 grammes of Cu_2S; CuS; Cu_2O; $CuO, CuSO_4$; $CuSO_4, 5H_2O$?

11. If one gramme of K is taken, how many grammes may be formed of KI; KCl; HKO; $KHCO_3$; K_2CO_3; K_2SO_4?

12. If one gramme of zinc is taken to make hydrogen, (*a*) how much sulphuric acid will be required? (*b*) How much H will be liberated? Its weight? Its volume? (*c*) How much $ZnSO_4$ will be formed? (*d*) How much $ZnSO_4,7H_2O$ may be crystallized out?

13. In making oxygen from K_2O, Cl_2O_5, what will be the weight of the products from 100 grammes? What, the volume of the oxygen?

14. Repeat these calculations with the reactions given for the manufacture of H_2S; CO_2; HCl; Cl; reckoning each as in Ex. 13 or in Ex. 12.

15. In the preparation of H_2O, N_2O_5 from 100 grammes of saltpeter, (*a*) how much H_2SO_4 is used when the salt remaining is $KHSO_4$? (*b*) How much when the salt remaining is K_2SO_4? (*c*) Suppose 147 grammes of H_2SO_4 were used, what would be the salt remaining? (*d*) Suppose that no loss occurred, what weight of nitric acid would be obtained? What volume? (*e*) Would there be any difference in these last two results whether 100, 150, or 200 parts of H_2SO_4 were taken?

16. How many grammes of FeS are required to form enough H_2S to precipitate 100 grammes of $CuSO_4$? Of $Bi(NO_3)_3$? Of $3H_2O, As_2O_5$? What will be the formula of the sulphides? Suppose the H_2S were passed into a solution of Fe_2Cl_6, how much sulphur would be precipitated?

17. Given this reaction, $2(PbO, N_2O_5) + K_2O, 2CrO_3 + H_2O = 2(PbO, CrO_3) + K_2O, N_2O_5 + H_2O, N_2O_5$, what will be the proportions taken and the products obtained? If one gramme of PbO, N_2O_5 is taken, what will be the weight of the others?

18. From the reaction given in § **212**, calculate how much of the two acids is necessary to dissolve one gramme of gold.

19. From the reactions in § **228**, calculate how much phosphorus can be made from 100 pounds of bone ash; then from 100 pounds of bones.

20. From the reactions given on p. 101, calculate the details of making 100 grammes of chlorate of potassa. (*a*) How much Cl is required? (*b*) How much NaCl? (*c*) How much H_2SO_4? (*d*) How much MnO_2? (*e*) How much KCl will be formed? (*f*) How can this last product be prevented from forming?

21. (*a*) How many cubic feet in a room 10 feet high, 15 feet long, and 12 feet wide? (*b*) How many cubic feet of oxygen does it contain? (*c*) How many pounds of burning charcoal will consume it completely, if it burns to CO_2? (*d*) How many pounds of burning charcoal will contaminate the air with five per cent of CO_2? (*e*) How long will it take one adult to contaminate it with two per cent of CO_2? (§ **302**). (*f*) How long will it take a gas burner consuming four feet of gas per hour to contaminate it with two per cent of CO_2? (*g*) How much fresh air should be admitted per hour so that, with the adult and the gas burner together, the air should not contain more than 0.5 per cent of CO_2? (*h*) Reckon the same from the size of your own bed-room.

22. Determine the atomic weight of chlorine from the following data: 100 grammes K_2O, Cl_2O_5 yield 60.939 grammes KCl; 22.032 grammes Ag (at. wt. 108) required 15.216 grammes KCl for complete precipitation (at. wt. $K = 39.1$), 14.427 grammes KCl gave 27.749 grammes AgCl.

23. 1.586 grammes pure Fe yield 2.265 grammes Fe_2O_3: calculate the atomic weight of iron.

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